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UNIVERSITY OF ALBERTA

CATALYTIC HYDROLYSIS
OF
CARBON DISULFIDE AND CARBONYL SULFIDE

by



SHIMIN TONG

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMICAL ENGINEERING

EDMONTON, ALBERTA

Fall 1992



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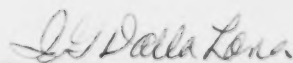
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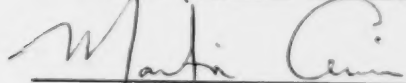
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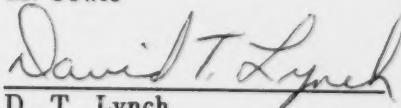
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ABSTRACT

The hydrolysis of carbon disulfide and of carbonyl sulfide, the removal of which is important for improving sulfur recovery efficiency in the modified Claus process, was studied using experimental approaches. The major work completed includes the following four aspects:

1. Experimental examination of commercial Claus catalysts to determine their relative activity for the hydrolysis of carbon disulfide;
2. Development of rate functions for the hydrolysis of both carbon disulfide and carbonyl sulfide on alumina and titania catalysts;
3. Computer simulation of the performance of alumina catalyst for the hydrolysis reactions in a Claus catalytic converter;
4. An investigation of metal promoters on the alumina to determine their effect upon catalytic activity for the hydrolysis reaction.

In the first part of the work, alumina-based catalysts (Kaiser 201, Kaiser 501), activated bauxite and a titania-based catalyst (CRS 31) were tested. A comparison of their activities is presented in chapter 3. The alumina-based catalyst (Kaiser 201) was found to have high activity for CS_2 and COS hydrolysis in the range of temperatures encountered in the first Claus converter. Even though the hydrophilic behavior of alumina (Kaiser 201) reduced its intrinsic rate compared with the less hydrophilic titania catalyst (CRS 31), its CS_2 and COS conversions was estimated to exceed 90% by simulation of a Claus converter.

The kinetic rate functions for CS_2 and COS hydrolysis were established on a representative alumina-based catalyst (Kaiser 201) and a titania-based catalyst (CRS 31). Through model discrimination and statistical analysis, the experimental

data from the study of the kinetics were best-described by an Eley-Rideal model for both the alumina catalyst (Kaiser 201) and the titania catalyst (CRS 31). The titania catalyst (CRS 31) showed a higher activation energy than the alumina catalyst (Kaiser 201). But its larger pre-exponential factor and smaller water adsorption constant (appearing in the parameters of the rate function) made the titania catalyst (CRS 31) exhibit higher activity in the ranges of temperature tested.

Based on the experimentally established kinetic rate functions, a simulation of the simultaneous kinetics of hydrolysis and the Claus reactions was pursued using a one-dimensional adiabatic Claus converter model. In a further development of the simulation, catalyst deactivation was considered. A "Uniform Poisoning Model" applied to a catalyst with 90 % loss of activity for CS_2 and COS hydrolysis predicted that for the moderate-aged alumina catalyst (Kaiser 201), 56 % conversion of CS_2 and 65 % conversion of COS may be expected. As the model predicted, increasing the operating temperature could increase CS_2 and COS conversions but would also reduce the equilibrium limiting conversion for the Claus reaction. Increasing the catalyst bed might also increase CS_2 and COS conversions, but it was not beneficial for additional Claus conversion. Calculations also showed that a modified geometry of the catalyst pellet could effectively improve the efficiency of the catalyst for CS_2 and COS conversions. A study of the effects of metal additives on alumina to form a dual function catalyst showed that a transition metal, iron, had the highest promotion effect on the activity for CS_2 and COS hydrolysis. The reducing gas, H_2S , hastened the transformation of the transition metal on the alumina to its corresponding sulfide and the activity was increased. The activity of the transition metals examined in this experiment related to their position in the periodic table and to their M-S bond strength.

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The author's greatest personal debt is to his wife, Yuqing, whose encouragement and unfailing patience were invaluable for the completion of this work. The author is also indebted to his mother-in-law for her motherly dedication by taking care of his lovely daughter, Cathy.

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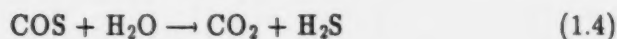
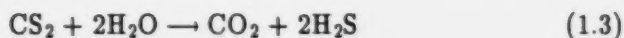
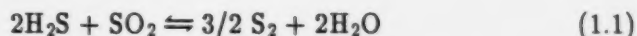
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CHAPTER 1

INTRODUCTION TO CS₂ AND COS HYDROLYSIS

1.1 INTRODUCTION

The continuing demand for sulfur and the increasingly stringent restrictions on sulfur-containing gas emissions has created a need for an improved Claus catalyst able to eliminate CS₂ and COS compounds. The presence of toxic CS₂ and COS compounds in the Claus tailgas lowers the sulfur recovery efficiency and, more importantly, creates environmental problems. Therefore, the conversion of CS₂ and COS compounds, generally produced in the front-end combustion chamber of the Claus unit, to sulfur is of increasing importance nowadays. Much emphasis has been placed on the improvement of Claus catalysts to enable their dual catalytic functions on both H₂S/SO₂ reaction (1.1) and the hydrolysis reactions (1.3) and (1.4).



In future, the removal of CS₂ and COS compounds from sources such as processing of high sulfur heavy oil and production of coal liquefaction products will become increasingly more important due to increasing concerns by the public regarding environmental issues.

The presence of hydrocarbons and carbon dioxide in the sulfur plant feed results in the production of the unwanted CS₂ and COS compounds in the combustion chamber of the Claus unit. Some new technologies for the removal of CS₂ and COS compounds in the Claus process have been suggested (Luinstra and d'Haene, 1988; Sulfur, 1990), among which the catalytic hydrolysis of CS₂ and

COS in the first Claus converter is still the most recommended (Grancher, 1978).

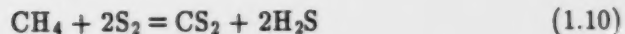
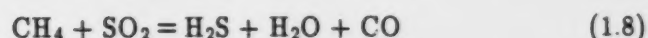
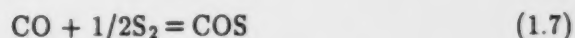
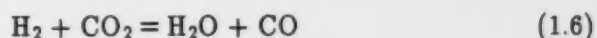
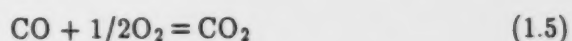
The catalysts currently used for the Claus process can be classified into two major types: alumina-based and titania-based. Although some plant performances (and manufacturer claims) (Claus Catalyst, 1986; Dupin, 1982) suggest that perhaps the titania-based catalyst is more active for the Claus conversion and the hydrolysis reactions than alumina-based catalysts, alumina catalysts continue to dominate the marketplace of North American sulfur recovery plants (up to 80%). Engelhard is currently marketing a new generation of bauxite based sulfur recovery catalysts: "SuReCat". Its suggested advantages are lower cost, better performance and long-term history of application of alumina catalysts in sulfur recovery plants.

Despite their importance, very little is known about the hydrolysis reactions involved in the Claus process. In this chapter, the prior background and experience relevant to the removal of CS_2 and COS compounds in the Claus process will be discussed.

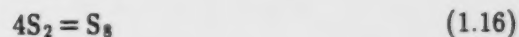
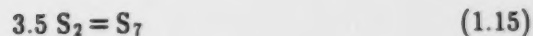
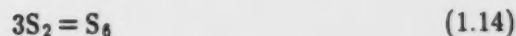
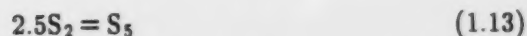
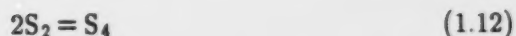
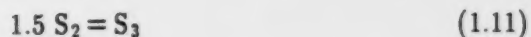
1.2 CS_2 AND COS COMPOUNDS PRESENT IN THE CLAUS PROCESS

Almost all of the elemental sulfur recovered from gas streams today is produced from hydrogen sulfide. This is usually done in two stages: the separation of an "acid gas" containing hydrogen sulfide from the original "sour gas" followed by the processing of the acid gas to convert the hydrogen sulfide to sulfur, usually by the Claus process. The source of "sour gas" can be natural gas, refinery gas or other industrial gases. After sweetening of the sour gas, the resulting acid gas is sent to the combustion chamber of the Claus unit. The composition of the acid gas is directly related to the nature of the sour gas processed and to the separation method employed. Processes using physical solvent may lead to an acid gas with

high hydrocarbon concentration if the source "sour gas" contains hydrocarbons (Sander, et al., 1984). Other impurities like carbon dioxide and ammonia may also be found in acid gas (Kerr, 1977; Grancher, 1978; Sander, 1984). When the process gas passes through the front-end combustion chamber, a large number of side-reactions take place apart from the desired reactions (1.1) and (1.2). In addition to the hydrolysis reactions (1.3) and (1.4), the most important overall reactions of this kind are the following:



and



The product sulfur and impurities, CO_2 and hydrocarbons (like CH_4), in the above reactions, in the feed are mainly responsible for the formation of CS_2 and COS . Since the removal of CO_2 and hydrocarbon from the process gas is economically limited, the CS_2 and COS compounds produced in the combustion chamber have

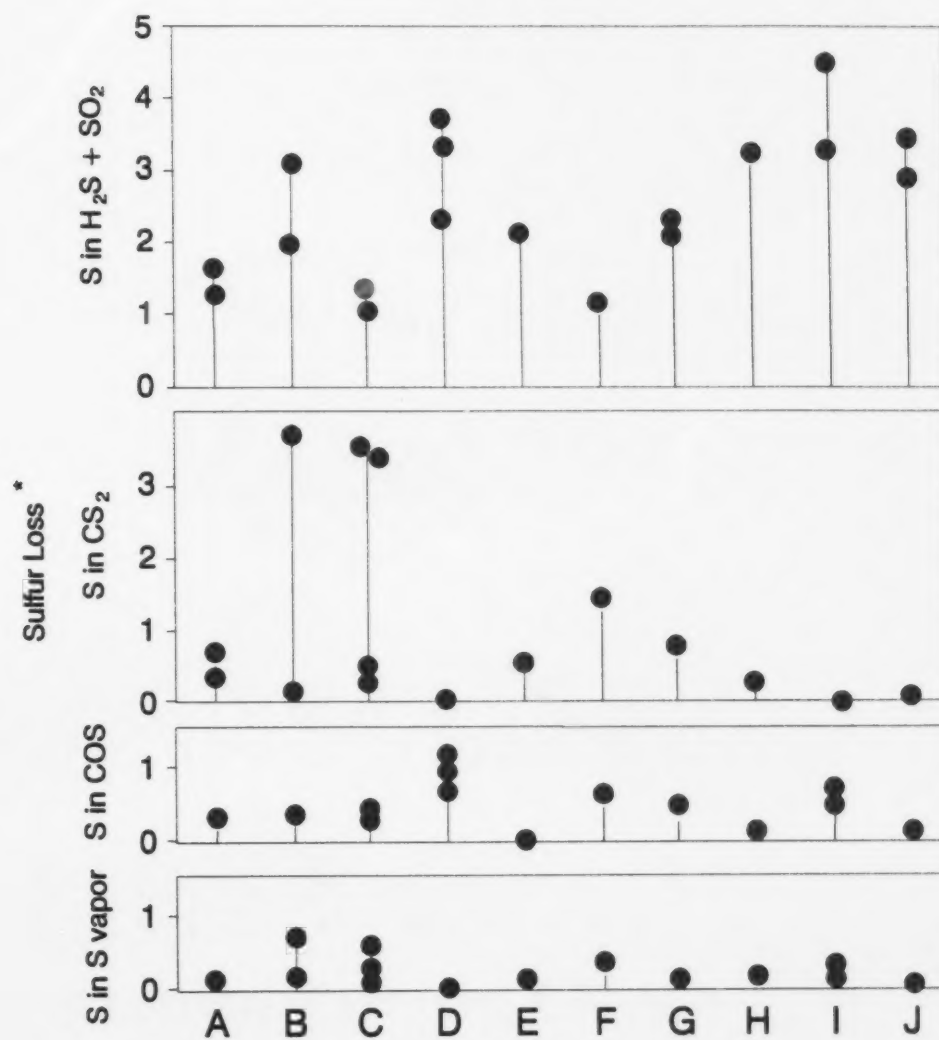
to be eliminated in the following Claus converters or, as a last resort, by using tail gas clean-up. Figure 1.1 illustrates the sulfur losses for ten Shell Canada recovery units operated in the Province of Alberta (Luinstra and d'Haene, 1988). In most cases, the greatest losses, about 2 to 3% of the acid gas feed, are due to H_2S and SO_2 . The second biggest contributor to losses is CS_2 , being over 3% in three cases. Although COS does not contribute to an effluent problem significantly as shown in Figure 1.1, significant amounts are produced in the combustion chamber. Its removal in the following Claus converters is comparatively easier than that of CS_2 . The fact that COS hydrolyzes more rapidly than CS_2 is discussed in the literature (Pearson, 1981; Dalla Lana, 1973).

1.3 TECHNOLOGY FOR ELIMINATING CS_2 AND COS COMPOUNDS

In the early history of the sulfur recovery industry (from the 1950's onward), the tail gas from a Claus plant was usually incinerated and then vented. In this treatment, the sulfur losses from these compounds were not recovered and the toxic compounds in the tail gas were released in the less offensive but still harmful form, SO_2 , to the atmosphere. With the more restrictive sulfur emission guidelines, the technology for purifying Claus plant tail gas was extensively improved during the 60's and 70's (Sander, 1984). Figure 1.2 illustrates how a number of important tail gas purification processes relate to a conventional sulfur recovery plant. It also shows the form in which they produce the recovered sulfur and the final purity of the waste gas that can be obtained by each method.

Although the use of improved tail gas purification technology can greatly relieve the sulfur emission load, it produces other problems. First of all, installing a tail gas clean-up unit involves high capital and maintenance costs. Secondly, periodic disposal of waste solid or waste solutions produces an additional pollution

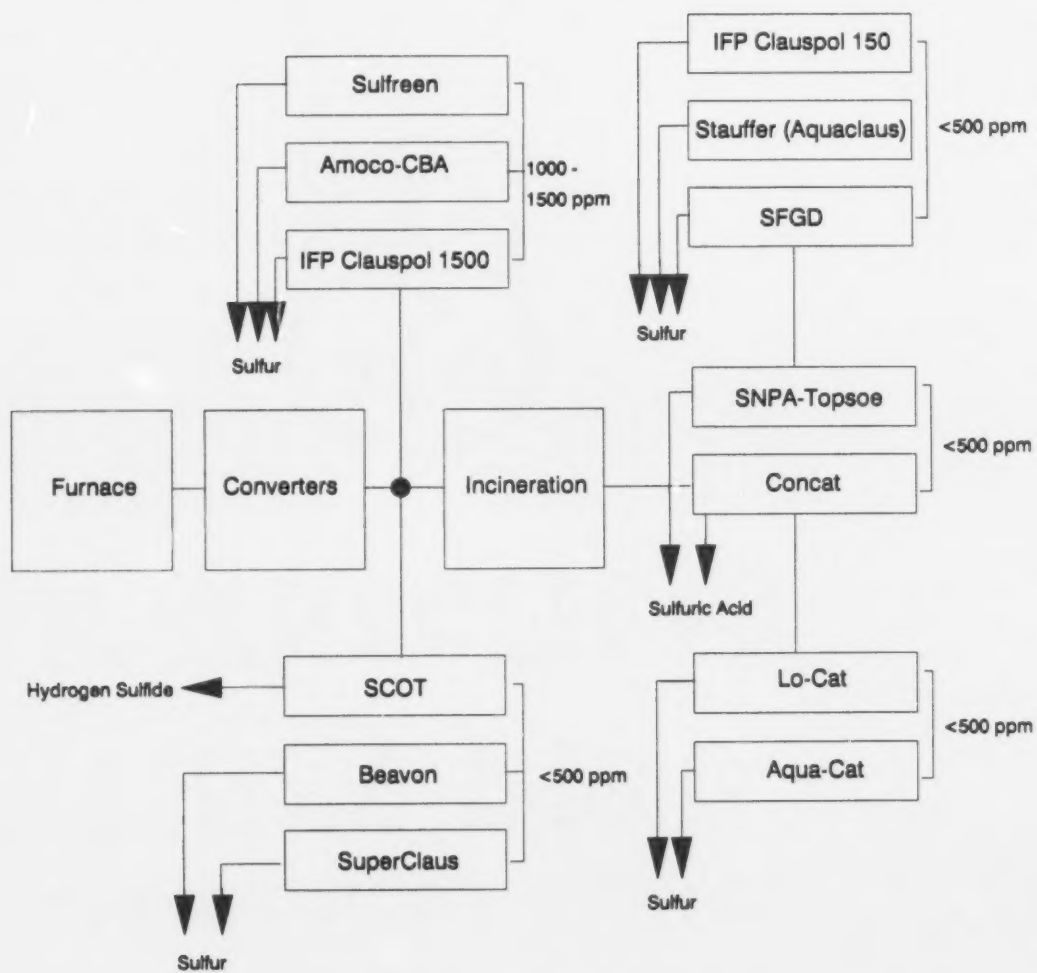
Figure 1.1 Tail Gas Sulfur Load in Ten Sulfur Recovery Units
in the Province of Alberta



* Sulfur loss as % S in feed

A, B, ...J: Different Sulfur Recovery Plants in Alberta

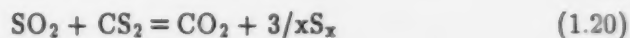
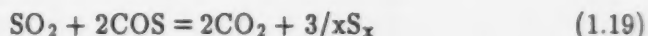
Figure 1.2 Tail Gas Purification Processes



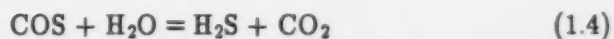
problem. The CS_2 and COS compounds may still exist in the vent gas. The ideal solution for the removal of CS_2 and COS compounds is the addition of promoters to Claus catalysts to enable them to catalyze the hydrolysis reactions (1.3) and (1.4), either in Claus converters or directly in the combustion chamber. It has been proposed that advantage be taken of the hydrogen in the Claus process gas to reduce sulfur-containing compounds to H_2S via reactions (1.17) and (1.18) in the first Claus converter with the help of a hydrogenation catalyst of the CoMo type (Grancher, 1978).



The resulting H_2S may be processed in subsequent steps of the Claus unit. However, under the operating conditions in Claus converters, where the SO_2 partial pressure is much higher than those of CS_2 and COS , it is SO_2 which is preferentially hydrogenated. Other possible reactions for the removal of CS_2 and COS are the following:



and



Dalla Lana et al. (1973) investigated the reaction (1.19) on an alumina catalyst. It was found that the alumina catalyst exhibited only initial activity towards the

reaction, and the conversion was observed to decline to a negligible level after 1.5 hours of online operation due to CO_2 poisoning. George (1974), however, reported that a cobalt-molybdate catalyst was active for the reaction (1.19) without CO_2 poisoning. This approach was unlikely to be accepted in Claus industry due to the high cost of the cobalt-molybdate catalyst. Publicly, more interest was focused on the hydrolysis reactions (1.3) and (1.4). The partial conversion of CS_2 and COS compounds in the Claus converters by the hydrolysis reactions is believed to be beneficial because of the favorable thermodynamic conditions and the high water content (15–30 %) available in the Claus converters. On a fresh alumina catalyst, the highest conversions of CS_2 and COS currently obtained in the first Claus converter are still of the order of 90 % for COS and 70–75 % for CS_2 (Grancher, 1978). Table 1.1 presents the reported hydrolysis conversions obtained under first converter conditions with a Claus gas containing 0.3% vol. COS, 0.3% vol. CS_2 and 500 ppm oxygen (Grancher, 1978).

Table 1.1 Temperature Effect on CS_2 Conversions (%)

Commercial Catalysts	Reaction Temperature	
	300°C	330°C
Activated Alumina No. 1	76.8	84.8
Activated Alumina No. 2	64.3	88.4
Old Activated Alumina	71.0	95.6
Specific Catalyst No. 1	85.5	99.8
Specific Catalyst No. 2	45.0	70.0
Old Activated Alumina No. 1 Plus AM Protection	80.3	95.3
Specific Catalyst No. 1 plus AM Protection	92.2	100

COS hydrolysis was complete in all tests. With the aging of the alumina catalyst, the hydrolysis activity declines. To maintain the high CS₂ and COS conversion, the reaction temperature must be gradually elevated with declining catalyst activity. Unfortunately, the H₂S/SO₂ conversion decreases with the increase of reaction temperature due to thermodynamic limitations. For example, the theoretical conversion for a typical converter gas stream gives 74.3% yield at 300°C compared with 57.6% yield at 350°C. In the subsequent second and third converters, negligible CS₂ conversion was reported (Grancher, 1978). It is commonly suggested that the hydrolysis of CS₂ and COS be executed in the first Claus converter by either raising the operation temperature or utilizing a more active specific catalyst. An economical yet more active specific catalyst is still not available to today's sulfur recovery industry.

Recently, a new method for the removal of CS₂ and COS directly in the Claus combustion chamber was reported by Luinstra and d'Haene working in Shell Canada Ltd (Luinstra and d'Haene, 1988). A honeycomb catalyst (Cordierite or Mullite) with or without alumina coating was installed in the Claus combustion chamber operated above 1000°C. In the best case, CS₂ and COS conversions of 99.5% and 65% were obtained, respectively. The work on selecting the best catalytic coating for the honeycomb and determining the stability of the catalytic activity under the Claus furnace condition was reported to be underway.

1.4 CS₂ AND COS HYDROLYSIS CATALYSTS

The importance of the activity of the Claus catalysts towards CS₂ and COS hydrolysis in the Claus converter was recognized during the 1970's because of the environmental restriction on sulfur emissions. Many new Claus catalysts were developed. The competition between the catalyst-producing companies

accelerated the rejuvenation of Claus catalysts for more efficiency and more durability. Activity for the removal of CS_2 and COS compounds became necessary for a Claus catalyst to be "good". During the 1960's, high purity alumina products were developed in France for use as Claus catalysts. Further developed in the United States, this new generation of alumina catalysts (spherical pellets) quickly began to replace traditional bauxite in new plants and replacement charges (Sulfur, 1990). Although the activity for the $\text{H}_2\text{S}/\text{SO}_2$ reaction was increased, other problems were encountered. The alumina catalyst was vulnerable to sulfation which lowers the catalyst activity, causing the converter efficiency to reach only one-half or one-third of the theoretical thermodynamic conversion limitation. Although alumina catalysts can catalyze CS_2 and COS hydrolysis, the conversion for CS_2 drops to only 50–60% after a few months and COS to a little more than 60%. To protect the high activities of the alumina catalysts for CS_2 and COS conversions, an AM-protection catalyst was developed by Rhone-Poulenc in the 1970's. The AM-protection catalyst is loaded on top of the alumina catalyst in each converter to eliminate oxygen and thus protect the underlying alumina from sulfation. This procedure has helped to improve converter performance. When used in the first converter, it noticeably improves CS_2 hydrolysis, but with drawbacks. Catalyst poisoning is not completely suppressed; contact time for all catalytic beds should be high to ensure high conversion; reactors are loaded with two catalysts; and, some precautions have to be taken during operation to prevent the "burning" of the AM catalyst because of its sensitivity to oxygen. The investigation of additives to improve the performance of the high-purity alumina catalysts was continued. Oxides such as titania, iron oxide, or silica were typically used. The amount of the additives added to the high-purity alumina to improve its activity is usually small, the

preferred concentration being between 1 and 8%. Various specific promoted alumina catalysts, claimed to be suitable for specific process feeds, were developed, but a satisfactory catalyst, which is good for both Claus conversion and CS_2 and COS removal, has still not been developed. In the 1980's, a new type of titania-based Claus catalyst was developed by Rhone Poulenc (Dupin and Vermeersch, 1982). The plant performance (manufacturer claims) suggests that the titania catalyst is more active for both the Claus reaction and hydrolysis reactions than the alumina catalysts currently used in Claus units (Claus Catalyst, 1986; Dupin, 1982). Compared to alumina, titania shows remarkable stability to aging and resistance to sulfur oxide poisoning, maintaining its high activity for CS_2 and COS hydrolysis. However, the titania catalyst has not replaced alumina-based catalysts used in the Claus industry, price being one of the major reasons. Ironically, bauxite, a type of Claus catalyst used in the early stages of Claus industry, has recently been rejuvenated in the United States. The Engelhard Company claims that its new generation of sulfur recovery catalyst, SuReCat (bauxite-based), occupies 80% of the U. S. sulfur recovery catalyst market and states that SuReCat has commercially been proven to be superior to additive-promoted alumina catalysts for Claus conversion and CS_2 and COS hydrolysis. An important modification being made is that the spherical-shaped bauxite is intentionally processed to shift its pore size distribution from the micropore to the macropore range. The micropores of the catalyst are found to be easily blocked by sulfur slurry (Burns, 1974) and thus, will not supply an active surface after the initial period of reaction. Therefore, the modification of pore distribution to the macropore ranges may minimize the sulfur blockage problem. In addition, it is also beneficial for intraparticle mass transfer. Table 1.2 lists some of the important commercial Claus catalysts, shows their main compositions,

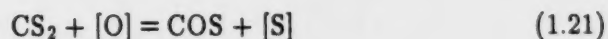
Table 1.2 Examples of Typical Claus Catalysts Used
in Sulfur Recovery Plants

Catalyst Notation	Catalyst Composition, wt%	Application	Origin of the Catalysts
S-201	Al ₂ O ₃ 93.6, SiO ₂ 0.02	Natural gas, Refinery Smelter	LaRoche Chemicals, Inc.
S-501	Fe ₂ O ₃ 0.02, Na ₂ O 0.35		
S-701	Al ₂ O ₃ 93.5, SiO ₂ 0.02 Fe ₂ O ₃ 0.02, Na ₂ O 0.45 Titania based		
		High efficiency to CS ₂ and COS Hydrolysis, lower sulfate	
R 10-11	Al ₂ O ₃ > 95, Na ₂ O <0.1, Fe ₂ O ₃ < 0.05	Claus plant with tail gas treatment	BASF AG
R 8-11	SiO ₂ 2.0, Na ₂ O <0.1 MoO ₃ 13.5, CoO 5,		
S-100	Al ₂ O ₃ 95.1, SiO ₂ 0.02, Fe ₂ O ₃ 0.02, Na ₂ O 0.30,	O ₂ enriched Claus plants Sub dew point tail gas unit	ALCOA
CR	Al ₂ O ₃ 94, Na ₂ O 0.5,	Resistant to carbon poisoning Resistant to sulfate, High efficiency to CS ₂ and COS hydrolysis	Rhône Poulenc
CRS 31	TiO ₂ >85		
CSR-2	Al ₂ O ₃ 93, Fe ₂ O ₃ 0.03, SiO ₂ 0.03, Na ₂ O 0.3,	Resistant to sulfuric acid, ammonia/amines	Catalysts and Chemicals Inc.
SuReCat	Al ₂ O ₃ 89, Fe ₂ O ₃ 2 TiO ₂ 2.8, SiO ₂ 6.2	Rich & lean acid gases	Engelhard

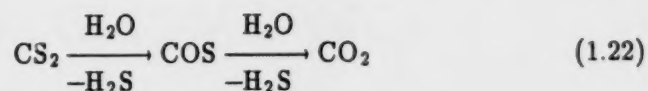
and their special application to different feed source conditions.

1.5 KINETIC STUDIES OF CS₂ AND COS HYDROLYSIS

Kinetic studies of the hydrolysis of CS₂ or COS or of the hydrolysis in the presence of other compounds found in the Claus process such as H₂S, CO₂, SO₂ and trace oxygen, are scattered in the literature (Tan et al., 1991; Guo and Zhang, 1988, 1986; Fiedorow and Dalla Lana, 1984; Akimoto and Dalla Lana, 1980, 1979; Chan and Dalla Lana, 1978; Kerr and Paskall, 1976, 1977; George, 1974). The experimental work by Pearson (1981) showed that COS hydrolysis is much faster than CS₂ hydrolysis. Under equivalent aging conditions, the conversion of COS is consistently much higher than that of CS₂ on both alumina based S-201 and titania based S-701. In the work by C. L. Liu et al. (1972), the formation of COS from CS₂ via reaction (1.21) on the alumina surface was observed in infrared spectral analysis of the gas-phase surrounding the catalyst wafer.



This evidence, combined with the above findings of Pearson (1981), may support the following consecutive reaction sequence:

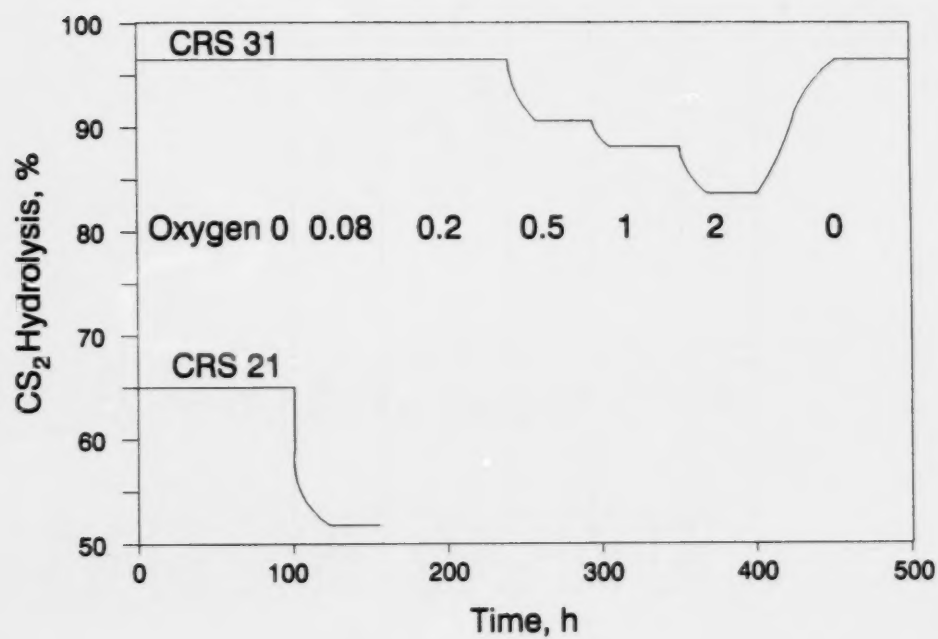


According to this consecutive reaction sequence, the effluent from CS₂ hydrolysis exhibits a typical sequence of CS₂, COS and CO₂ concentration with contact time, and the catalyst is able to accelerate both CS₂ and COS hydrolysis. Some common

features between CS_2 and COS hydrolysis have been observed in previous work. The basicity on alumina surfaces appears to be the active center for both CS_2 and COS hydrolysis (George, 1974; Akimoto and Dalla Lana, 1980; Fiedorow et al., 1984). The compounds, CO_2 and H_2S , which do not affect the COS hydrolysis rate, do not affect the CS_2 hydrolysis rate either (Akimoto and Dalla Lana, 1979; Tong et al., 1992). Both CS_2 and COS hydrolysis rates are first order in CS_2 and COS concentrations and zero order in H_2O concentration when the gas-phase water concentration is sufficiently high (Zhang and Guo, 1988; Kerr and Paskall, 1976). These common features demonstrate the similarity in kinetic behavior between CS_2 and COS hydrolysis.

The activation energy for CS_2 or COS hydrolysis tested on alumina catalysts is also surprising low (<10 kcal/mol) and consistent results were obtained from various sources (George, 1974; Fiedorow et al., 1984; Zhang and Guo, 1988; Tong et al., 1992). However, in Claus converters, the activity for CS_2 and COS hydrolysis on alumina catalysts is not evident like that in controlled hydrolysis studies. Aside from the normal thermal and hydrothermal degradation, physical attrition and carbonization, sulfation of the catalyst in the commercial Claus process is considered to be responsible for the cause of activity loss (Zhang and Guo, 1986, 1988; Pearson, 1978). Sulfation, although its mechanism has not yet been positively identified, appears to be related to the excess of oxygen and SO_2 in the system. When titania CRS 31 catalyst is used, the activity loss for CS_2 hydrolysis due to excess oxygen is reversible, unlike that with an alumina-based catalyst. Typical experimental evidence is shown in Figure 1.3 (Dupin, 1982). A possible explanation is that in contrast to alumina, which reacts with sulfur oxides to form aluminum sulfate such as $\text{Al}_2(\text{SO}_4)_3$, the sulfates of titanium dioxide such as $\text{Ti}(\text{SO}_4)_2$ and TiOSO_4 are unstable at the temperature used in Claus converters.

Figure 1.3 Comparison of the Effect of Oxygen on CS₂ Hydrolysis
on Alumina (CRS 21) and titania (CRS 31)



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It is well known that the surface state of a catalyst will affect the activity of the catalyst, but it is not yet clear how the surface state of alumina affects CS_2 and COS hydrolysis. Evidence of CS_2 and COS adsorption on alumina surface under free water conditions was observed by Nemeth and Gati (1990). When water vapor is present in the system, it is very difficult to check experimentally whether CS_2 and COS are adsorbed on the alumina surface. Therefore, whether the hydrolysis of CS_2 and COS proceeds via adsorption of CS_2 and COS has still not been positively identified.

1.6 PROMOTERS AND POISONS OF CS_2 AND COS HYDROLYSIS

In the Claus process, a catalyst that displays high activity for the Claus reaction is not necessarily active for CS_2 and COS hydrolysis even though thermodynamics indicate near 100% conversion is possible. Usually, 50–60 % conversion of CS_2 on a moderate-aged alumina catalyst is attained. The requirement for higher sulfur recovery, pressure from the public concerning the environmental issues, and the realization of the difficulties in the Claus process for total removal of CS_2 and COS have spawned studies to consider the effects of promoters and poisons on the supported Claus catalysts. Efforts have been focused on the compounds, encountered in the Claus process gas, such as oxygen, sulfur dioxide, hydrogen sulfide and carbon dioxide as well as carbon, sulfur and ammonia, for their influence on the Claus conversion and hydrolysis reactions. Additives such as iron oxide, titanium oxide and silica are typically used to improve the performance of the alumina catalysts. The studies of NaOH as a basicity promoter for alumina catalysts have also been found in the literature (Fiedorow et al., 1984; George, 1974).

Carbon deposition may accumulate on the top of the catalyst, which

deactivates the catalyst by site blocking and pore plugging. The carbon crust itself does not appear to poison the catalyst seriously (Kerr and Paskall, 1976). Its potential for reaction with elemental sulfur and hydrogen in the Claus converter to form a polymer tar is present, which could seriously deactivate the catalyst. Coking rates vary in proportion to the molecular weight of the feed. The acid gas from heavy petroleum causes rapid coke accumulation because of the high concentration of heavy hydrocarbon molecules. The cracking of CS_2 and COS is also a source of carbon deposition on the catalyst surface.

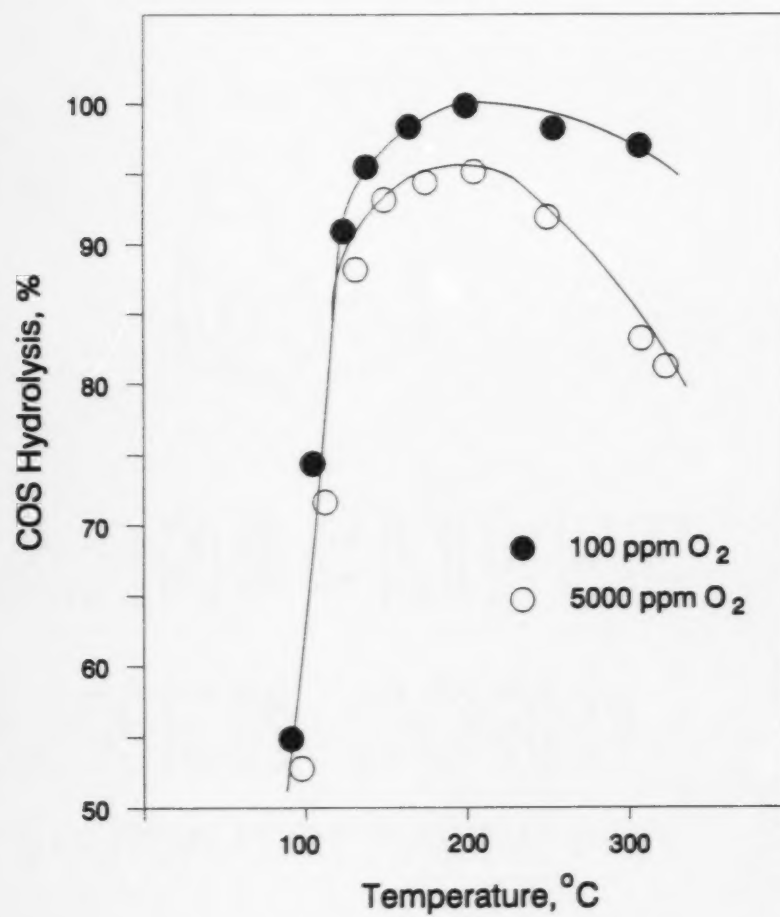
Sulfur accumulation on the catalyst significantly depends on the operating temperature used. From a thermodynamic point of view, lower operating temperatures favor high equilibrium Claus conversions. But the high sulfur dew point limits the minimum operating temperature. Even with an operating temperature carefully controlled above the sulfur dew point, sulfur fouling is still unavoidable. Sulfur can still be retained on the catalyst surface strongly enough to deactivate an appreciable proportion of the active sites. The degree of sulfur poisoning depends on the concentration of sulfur-containing species in relation to the operating temperature, and perhaps, by the catalyst pore structure.

Sulfation is probably the most significant cause of catalyst activity loss in the Claus process. This results from the presence of oxygen in the process gas which forms sulfate surface species on alumina catalysts. The extent of the decline of the CS_2 conversion activity is related to the sulfate content formed on the catalyst (Guo and Zhang, 1986; Pearson, 1978). However, the sulfate, whether it comes from adsorbed sulfur dioxide or from traces of sulfur trioxides, has not been positively identified. The H_2S itself does not affect CS_2 or COS hydrolysis, but it could assist the deactivation process of the hydrolysis reaction when oxygen exists in the system. Figure 1.4 shows evidence of H_2S poisoning action on the hydrolysis

Figure 1.4 Effect of Temperature on Catalyst Activity
When Oxygen is Present in the System

Test Condition:

COS = 1.5 mol %, COS/H₂S = 30/1, H₂O = 1.5 mol %



Cuei Hua Xue Bao, 9, 132 (1988)

reaction when traces of oxygen are present (Zhang and Guo, 1988). The conversion of COS declines significantly above 200°C when the oxidation of H₂S to SO₂ becomes significant. Thus, the coexistence of SO₂ and O₂ results in sulfation on the alumina catalyst. On the titania-based catalyst, CRS 31, the poisoning due to the introduction of oxygen is reversible. The instability of sulfate on a titania surface under the operation temperature in a Claus converter may well explain the reversible phenomenon.

Few literature sources describe the study of promoters even though many promoted Claus catalysts, each with a special code name, have been commercialized. George (1974) investigated the effect of NaOH, which was loaded on Chromosorb-A and Cobalt-molybdate catalysts, on the hydrolysis of COS. The rate of COS hydrolysis was found to be increased by the presence of a base (NaOH) on the catalyst surface. Surface basic sites, being considered the catalytic active centers, have been reported by several authors (Akimoto and Dalla Lana, 1979; George, 1974). The NaOH additive could enhance alumina surface basicity sufficiently to increase the hydrolysis activity. But when NaOH is overloaded on the alumina surface, the activity for CS₂ hydrolysis is found to be inferior to that of unpromoted alumina catalyst (Chapter 7). Iron, as a promoter for Claus catalysts, has not been mentioned in the literature for its possible function in the hydrolysis of CS₂ and COS. Up to date, finding a catalytic promoter for the hydrolysis of CS₂ and COS, one highly resistant to the sulfation in the Claus process, has been challenging.

1.7 SCOPE OF THE PRESENT WORK

This survey reveals that much effort has gone into improving the efficiency of Claus catalysts for sulfur recovery. The CS₂ and COS conversions, important to

the increase in sulfur recovery efficiency, do not occur easily in Claus converters as indicated by the harsh processing conditions and complex feed sources. At a more fundamental level, little is known about the CS_2 and COS hydrolysis reactions on industrial Claus catalysts. Although two types of Claus catalysts, alumina-based and titania-based, have been commercialized, and manufacturers claim that titania CRS 31 is more active than alumina catalysts, this has not yet been quantified. Whether the catalytic promoters which can elevate Claus conversions are also good for hydrolysis remains uncertain.

The purpose of this study is to use a Berty-type laboratory reactor to investigate some commercial Claus catalysts, both the alumina-based type and the titania-based type for their comparative hydrolysis activity as well as their chemical and physical differences. In particular, we want to identify how the two types of catalysts exhibit different kinetic behavior by establishing the appropriate forms of hydrolysis rate equations. Using these rate equations, a simulation study was employed to demonstrate the catalyst efficiency for CS_2 and COS conversion in a typical Claus process catalytic converter. This research also sought to measure the influences of mass transport on the performance of alumina catalyst, active or deactivated, for different physical geometries. Several alumina catalysts were modified by impregnation with iron, zinc, copper and sodium oxides and were tested for their function as hydrolysis promoters.

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CHAPTER 2

EXPERIMENTAL EQUIPMENT AND OPERATING PROCEDURES

2.1 EXPERIMENTAL EQUIPMENT

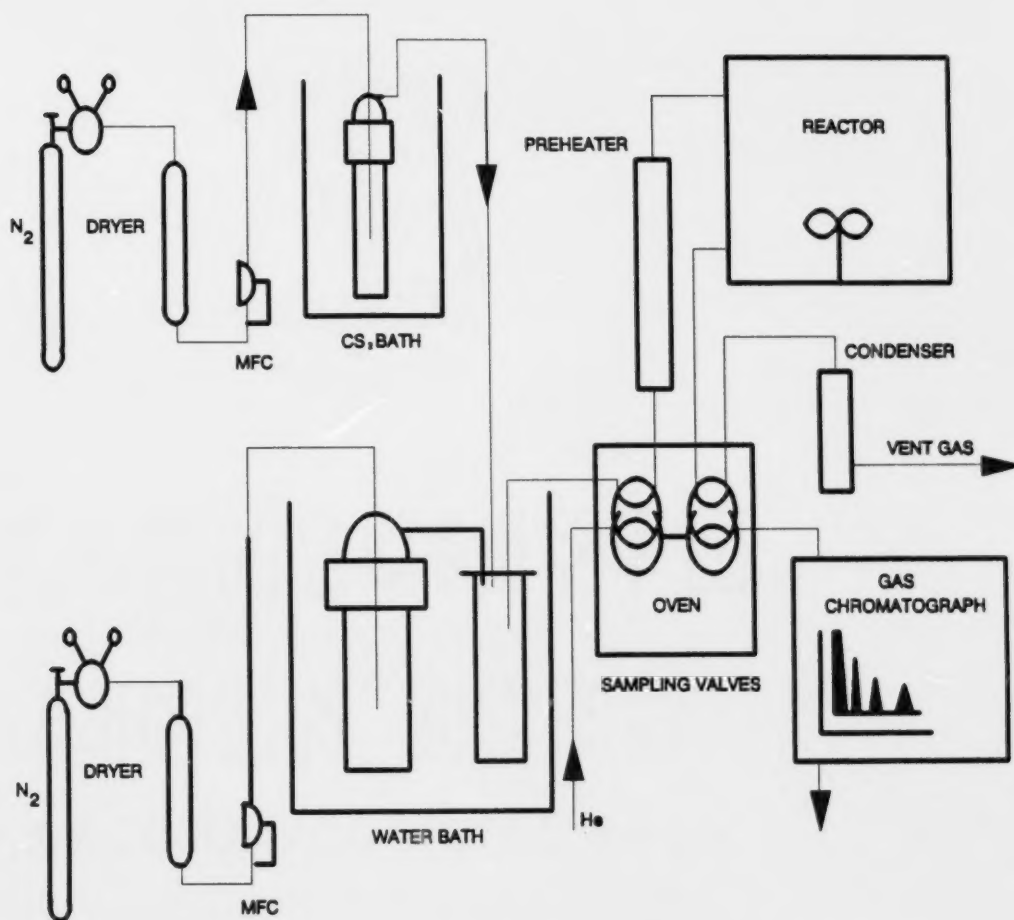
The reaction compounds for this study were carbon disulfide (CS_2 , analytical reagent, >99.9%, obtained from BDH Inc., Edmonton Sales Office), carbonyl sulfide (COS , calibrated 5 mol % $\text{COS}/95$ mol % N_2 gas mixture, obtained from Matheson, Edmonton), and ion-free water. A Berty reactor (21 cm diameter x 19 cm height) was used for undertaking the catalytic reaction studies. The experimental system was composed of three sections: feed, reaction, and feed and product analysis sections. A schematic diagram of the apparatus is shown in Figure 2.1. The unit was automated for control of reactor pressure, reactor temperature, bath temperature and for sampling compartment temperature.

2.1.1 Feed Section

The feed system was designed to supply the reactor with a gas stream of reactants at a constant flowrate and composition for long operating periods. It was desirable to change the feed composition to the reactor and still maintain the total feed stream flowrate constant.

Nitrogen gas (high purity, >99.9 %) was obtained in 2500 psig cylinders from the Linde Division of Union Carbide. The two nitrogen flows were maintained by mass flow meters. The feed components, H_2O and CS_2 , were introduced by saturating two streams of high purity nitrogen with either H_2O or CS_2 . The H_2O was held in a 1000 mL container immersed in a large water bath, controlled with a Thermomix 1420 regulator. The CS_2 liquid was contained in a 1000 mL vessel which was cooled in a refrigerated bath with 50 % diethylene glycol as coolant. The saturation degree of CS_2 and H_2O in the nitrogen streams was checked by bubbling the nitrogen streams through one H_2O (or CS_2) container and two H_2O (or CS_2) containers in series. H_2O and CS_2 peak areas were measured,

Figure 2.1 Schematic Diagram of Experimental Apparatus



respectively. The detailed procedure can be found in Appendix A. The refrigerated bath temperature could be maintained as low as -40°C . The two streams of nitrogen gas saturated with H_2O and CS_2 , respectively, were mixed to form the feed stream to the reactor.

Figure 2.1 Schematic Diagram of Experimental Apparatus

The required nitrogen flowrate for a certain feed composition in the experiment was calculated using the following four equations:

$$F_{\text{N}_2}^1 = X_{\text{CS}_2} F_t \frac{P_t - P_{\text{CS}_2}^0}{P_{\text{CS}_2}^0} \quad (2.1)$$

$$F_{\text{N}_2}^2 = X_{\text{H}_2\text{O}} F_t \frac{P_t - P_{\text{H}_2\text{O}}^0}{P_{\text{H}_2\text{O}}^0} \quad (2.2)$$

$$\ln P_{\text{H}_2\text{O}}^0 = 18.871 - 5288.80/T \quad (2.3)$$

$$\ln P_{\text{CS}_2}^0 = 22.541 - 3521.94/T \quad (2.4)$$

Equations (2.3) and (2.4) are obtained from the regression of data presented in Handbook of Physics and Chemistry (63rd edition, D-196 and D-204). The detailed establishment of above equations is also shown in Appendix C. Sample set points for the various feed compositions at a constant system pressure and total feed flowrate, $0.03 \text{ m}^3/\text{h}$, are presented in Table 2.1. Using different combinations of left and right sides of Table 2.1 for the set points, a total of 24 different feed compositions could be prepared.

In studying COS hydrolysis, the branch of the nitrogen gas stream used to saturate CS_2 vapor was replaced by a 5 vol % COS-nitrogen stream (mixture supplied by Matheson, Edmonton). Different feed compositions were obtained by blending the two streams of gas.

2.1.2 Reaction Section

The reactor was a 21 cm diameter x 19 cm height internal circulating Berty type reactor. The reactor inside volume was about 800 mL with catalyst bed size of 3.8 cm (i.d.) x 8.9 cm (height). The catalyst loaded was sparsely distributed on a stainless-steel mesh. The internal agitation provided by a sealed MagneDrive, belt-driven by a variable V*S Reliance Motor. The rotation speed was measured using a magnetic pickup coil. A high temperature furnace surrounded the top of the Berty reactor, and both the furnace and the bottom of the reactor were

Table 2.1 Experimental Variables

$F_t = 0.03 \text{ m}^3/\text{h}$, $P_t = 150 \text{ kPa}$

H ₂ O Bath Temp. °C	MFM Set %	$F_{N_2}^1$ m ³ /h	H ₂ O in Feed mol %	CS ₂ Bath Temp. °C	MFM Set %	$F_{N_2}^2$ m ³ /h	CS ₂ in Feed mol %
26.0	20.3	0.0267	2.0	-12.54	18.9	0.00251	0.5
38.2	19.9	0.0261	4.0	1.55	17.8	0.00236	1.0
45.8	19.4	0.0255	6.0	6.42	17.2	0.00228	1.25
59.7	18.0	0.0237	12.0	10.52	16.7	0.00221	1.50
				14.09	16.1	0.00213	1.75
				17.25	15.6	0.00206	2.00

$F_{N_2}^1$ — Nitrogen flowrate for saturating H₂O.

$F_{N_2}^2$ — Nitrogen flowrate for saturating CS₂.

insulated to provide better temperature control. The furnace temperature was monitored by three thermocouples located at different sections of the furnace. The top and side temperatures of the furnace were regulated independently. The

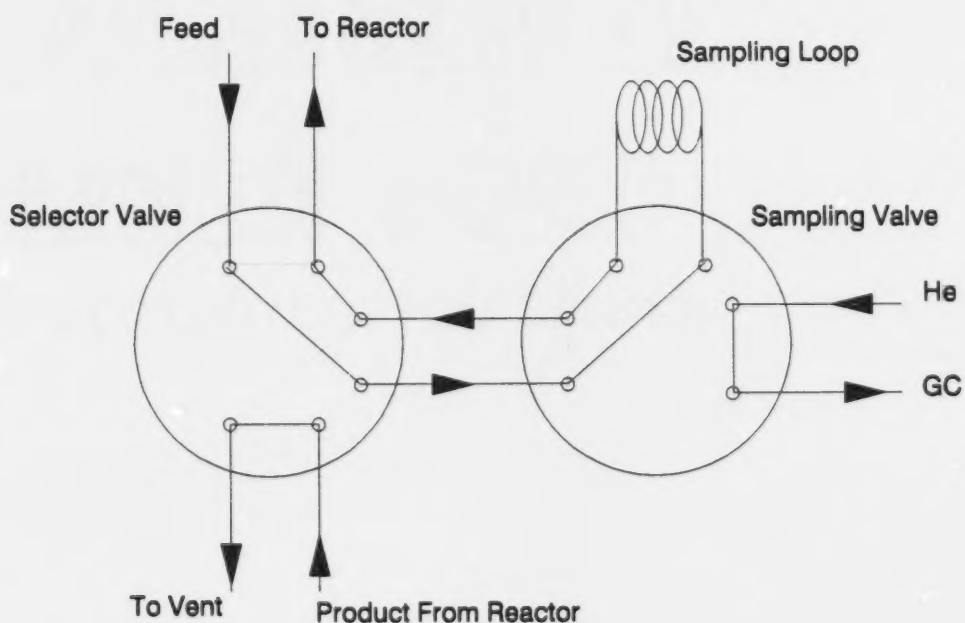
catalyst bed temperature was measured using a thermocouple directly touching the solid catalyst bed with the output shown on a multipoint recorder. The reactor pressure was controlled by a feedback—pressure control loop at 150 kPa.

The feed stream was preheated and then fed into the Berty reactor. The product stream was passed through the sampling box and then vented.

2.1.3 Feed and Product Analysis Section

Both feed and product streams were analyzed using a Hewlett—Packard on—line gas chromatograph (Model 1024) with thermal conductivity detector. The two streams continuously flowed through the stream selector valve which was housed in a thermostatted compartment. A diagram of the configuration of feed and product streams through the stream selector and sampling valves is shown in Figure 2.2.

Figure 2.2 Feed and Product Sampling System



The stream selector valve positions allow either the feed stream or the product stream to flow through the sampling loop of the sampling valve. The volume of gas trapped in the sampling loop was carried to the GC column for analysis by switching of the sampling valve. The column and the operating conditions for gas-phase chromatographic separation are given in Figure 2.3.

The sampling valve and stream selector valve were housed in a heated oven kept at 100°C to prevent condensation of water vapor and to insure the reproducibility of the sampling gas volume in the sampling loop. The calibration factors, defined by equation (2.5), for the compounds to be quantitatively analyzed were obtained by the following method.

$$f_i = \frac{\text{ith Component Concentration, mol \%}}{\text{ith Component Peak Area in GC Analysis}} \quad (2.5)$$

A 100 mL cylinder was first pressurized with high purity H₂S, CO₂ or COS gas. Then, the cylinder gas was diluted by further pressurizing using high pressure nitrogen to obtain the desired composition in the cylinder. The composition in the cylinder was calculated by weighing the cylinder after each gas was introduced. By using different quantities of H₂S, CO₂ or COS pressurized in the cylinder, mixtures with different concentrations could be obtained. This cylinder was then connected to the process line, enabling the gas stream with known concentration to pass through the sampling loop and to be analyzed by the gas chromatograph. The response peak areas were plotted against the concentrations of the sampling gas, the plot of which is shown in Figure 2.4 together with R square examination. All the R square values over 0.99 indicate that the relationship between the gas phase concentration analyzed and GC peak area is well represented by a linear correlation. The calibration factors between the peak area and concentration were

Figure 2.3 Gas Chromatogram

Column: 3m x 3mm Porapak QS

Detector: Thermal Conductivity

Regulator Pressure: 60 psig

Flowrate: 40 mL/min.

Oven Temperature: 60°C for H₂S, COS and CO₂ Analysis

Oven Temperature: 130°C for H₂O and CS₂ Analysis

Sampling Loop: 0.5 mL

Chromatogram

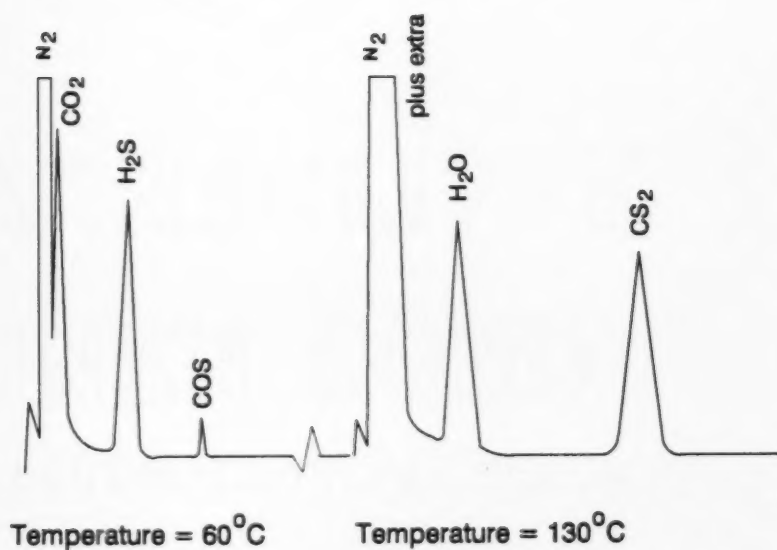
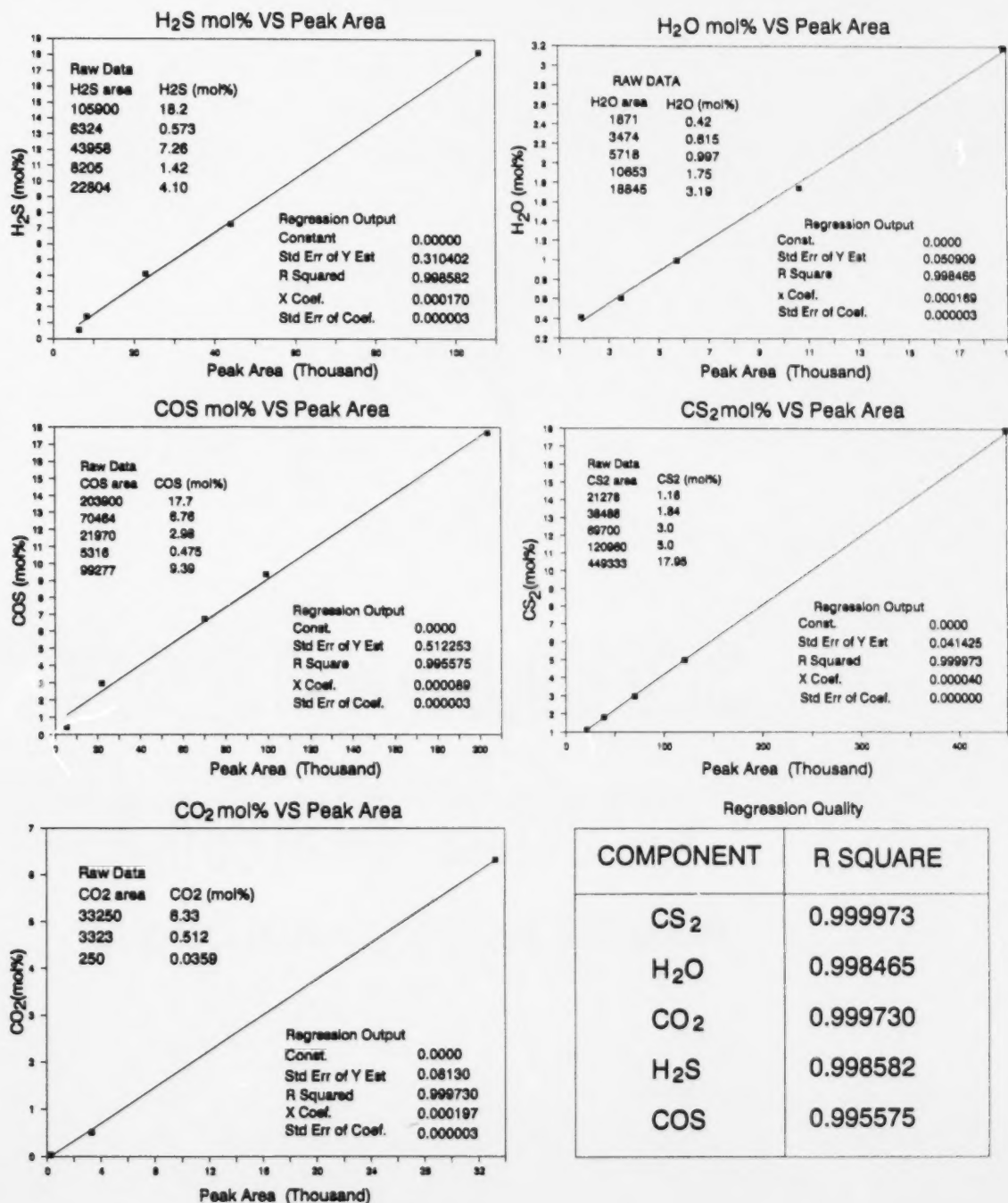


Figure 2.4 Component GC Peak Area Versus Its Concentration
of H_2S , COS , CO_2 , H_2O and CS_2



obtained through linear regression analysis. The GC calibration factors for water vapor and CS₂ vapor concentrations were obtained by a method similar to that for H₂S, CO₂ and COS gases, but the on-line concentrations passing through the sampling loop were calculated using the saturation vapor pressure of either CS₂ or H₂O in the nitrogen stream.

Table 2.2 presents the calibration factors used in this study. With these factors, the mol percent of each component, in either feed or product, can be calculated by multiplication of the GC peak area by its corresponding calibration factor. The calibration of the gas chromatograph was checked by making up an CS₂, H₂O and N₂ mixture of known composition and running this chromatogram at least once a week during the more active periods of the research program.

Table 2.2 Gas Chromatography Calibration Factors

Component	H ₂ S	COS	CO ₂	H ₂ O	CS ₂
Calibration Factor, f_i	1.70×10^{-4}	8.90×10^{-5}	1.97×10^{-4}	1.69×10^{-4}	4.00×10^{-5}

2.2 OPERATING OF EQUIPMENT AND EXPERIMENTAL PROCEDURES

Prior to starting the CS₂ and COS hydrolysis experiments, a blank test for the reaction system was performed. At 350°C and concentration of either 1 mol % CS₂ or 1 mol % COS and 2% H₂O, the difference between the inlet and outlet concentrations was found to be negligible, showing that the 316 stainless steel wall of the Berty reactor had no catalytic activity towards the hydrolysis of CS₂ or COS. The stirring speed of the reactor operation was then determined. As shown

in Figure 2.5, CS_2 conversion approaches constant when the agitator was driven at a stirring speed of over 1000 rpm. This suggests that the external mass transfer limitation is eliminated and the reactor reaches ideal mixing if the CS_2 hydrolysis tested is a first order reaction. When testing catalyst activity, the reactor stirring speed was set at 1100 rpm. Autoclave Engineers Inc. recommend operation of their Bertie reactor at higher gas densities (elevated pressures) to ensure that ideal recirculation (mixing) is achieved. In these studies, operation at more elevated pressures was not possible because of the vapor pressure restriction of the CS_2 and the water in preparing feed compositions. Compression of the feed gas stream was also not possible. Nonetheless, the good reproducibility of the various runs using the Bertie reactor and the fact that the experiments suggest that internal and external mass transfer limitation were eliminated enable one to have confidence that non-ideal mixing effects were not present.

After loading a fresh batch of catalyst, the reactor temperature was raised to 300°C and held there for 24 h with only a small nitrogen flow to ensure reaching a uniform reactor temperature. The CS_2 and H_2O bath temperatures were set at one of the desired points shown in Table 2.1. The catalyst surface was then exposed to the $\text{CS}_2/\text{H}_2\text{O}/\text{N}_2$ feed flow in the CS_2 hydrolysis experiment or the $\text{COS}/\text{H}_2\text{O}/\text{N}_2$ feed flow in the COS hydrolysis experiment. The hydrolysis reaction took place and was maintained for at least 5 h until the catalyst activity stabilized. These tests are presented in Chapter 3. After the reaction reached steady-state, which was confirmed from catalyst bed and reactor wall thermocouple readings, the feed and reactor absolute pressure transducer readings and component chromatography areas, the product compositions were analyzed once per hour. A total of five samples was taken for each experimental point, the average value of the hydrolysis conversion and reaction rates being used. Data

Figure 2.5 Influence of Internal Gas Recirculation

Test Condition:

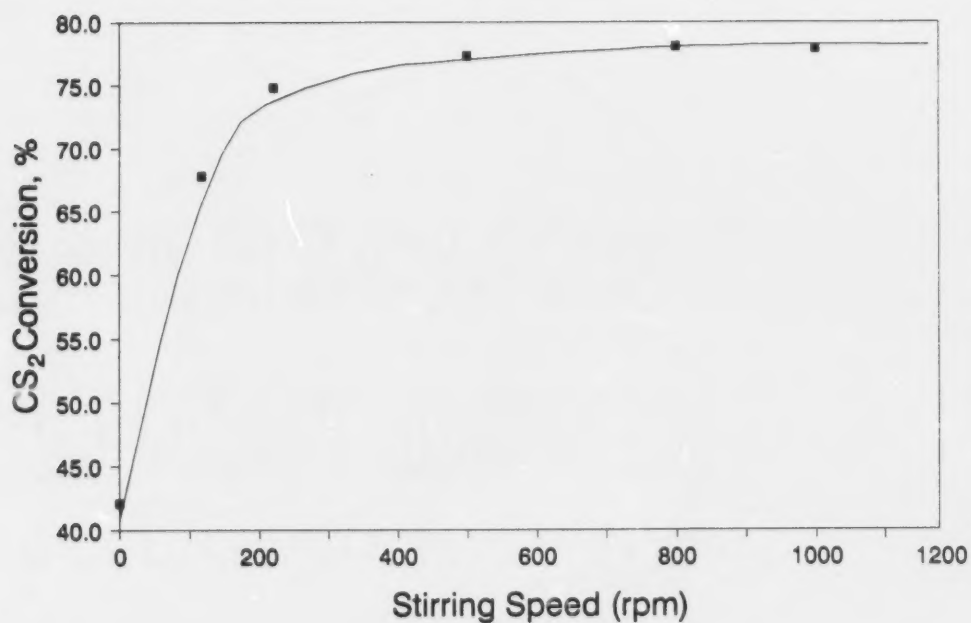
Reaction Temperature = 300°C

Reactor Pressure = 150 kPa

Feed Flowrate = 0.03 m³/h

Feed Composition, mol %: CS₂ = 1.09, H₂O = 2.05, N₂ = 96.86

Catalyst: 2 g CRS 31



reproducibility analysis using a "Minitab" package indicates that the standard deviation in conversion level is less than 0.02 as determined in appendix B, which leads to rate measurement maximum standard deviation of 0.00006 mol/g·h. At the end of a series of runs, the reactor was kept hot, but the CS₂ and H₂O or COS and H₂O gas stream were turned off. A small stream of nitrogen was run through the entire system until the reactor had cooled to room temperature.

2.3 NOMENCLATURE

f_i	=	Calibration factor of ith component, mol %/(peak area)
$F_{n_2}^1$	=	Nitrogen flowrate for saturating H ₂ O, m ³ /h
$F_{n_2}^2$	=	Nitrogen flowrate for saturating CS ₂ , m ³ /h
F_t	=	Total feed flowrate, m ³ /h
MFM	=	Mass flow meter seting, %
P_t	=	System pressure, kP _a
$P_{cs_2}^o$	=	Saturation vapor pressure of CS ₂ , kP _a
$P_{H_2O}^o$	=	Saturation vapor pressure of H ₂ O, kP _a
T	=	Temperature, K
X_{cs_2}	=	CS ₂ concentration in feed, mol %
X_{H_2O}	=	H ₂ O concentration in feed, mol %

CHAPTER 3

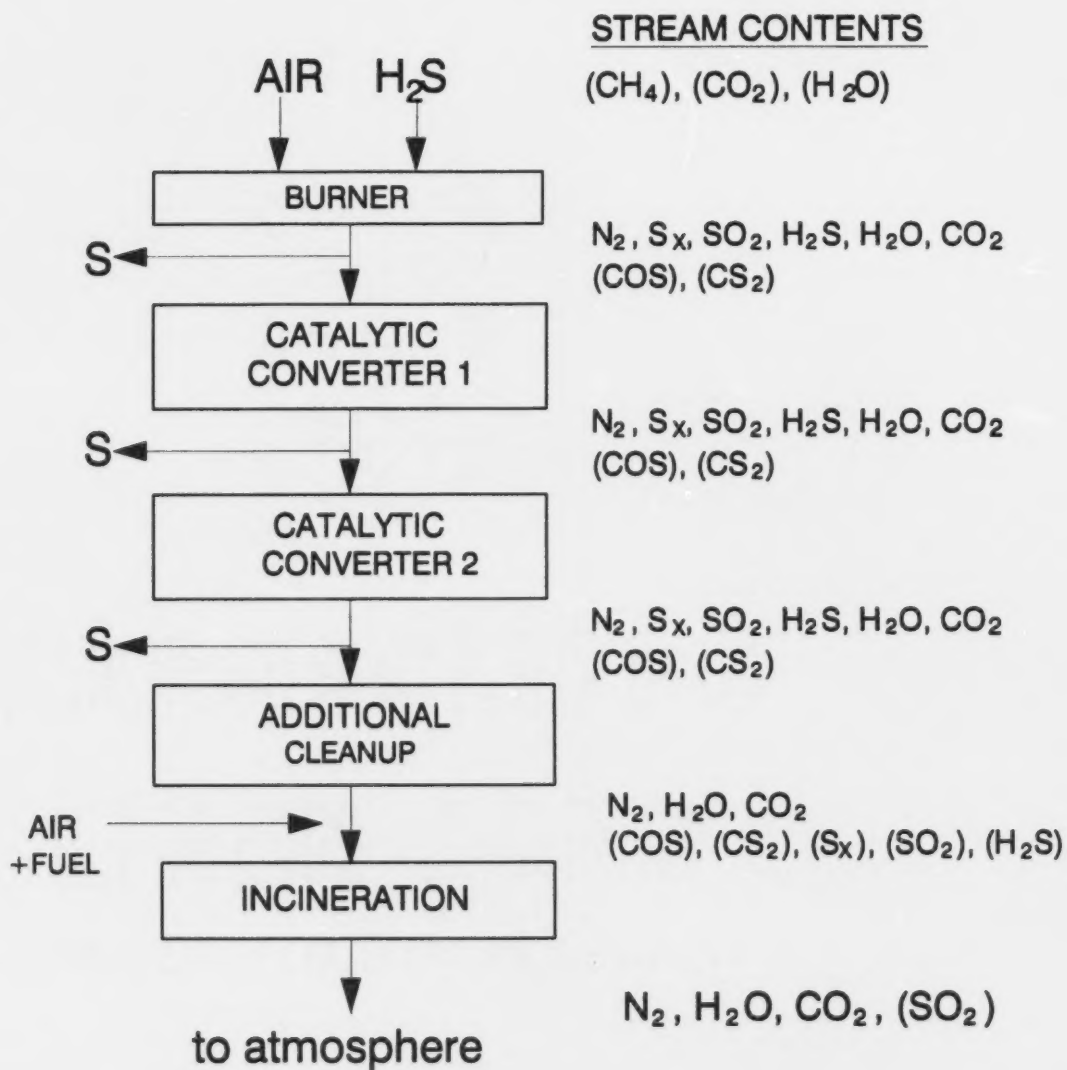
EVALUATION OF CATALYSTS FOR THE HYDROLYSIS OF CARBON DISULFIDE

3.1 INTRODUCTION

The removal of CS_2 and COS within modified Claus sulfur recovery plants meets varying success even today. Over decades of effort, various techniques for the removal of CS_2 and COS have been proposed and investigated but, aside from reduction to H_2S using hydrogen, to date no satisfactory and inexpensive method has solved the problem satisfactorily. With the current demanding environmental emission restrictions, the issue of CS_2 and COS removal must be reconsidered on the basis of both economics and effectiveness.

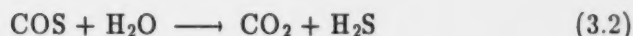
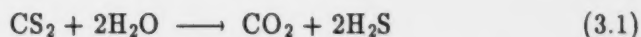
Figure 3.1 summarizes the process steps in a typical modified Claus plant. It is composed of a front-end burner, catalytic converters, and additional tailgas cleanup and incineration sections. The compounds shown on the right side of Figure 3.1 represent the normal constituents encountered at the inlet and outlet of each stage. The compounds in brackets are problem compounds, usually formed from impurities in the acidgas feed, that still must be removed in the following stage. As shown, if COS and CS_2 , produced in the burner, are not eliminated in the first or second converter, they may represent a significant sulfur loss and create a corresponding environmental problem. The widely accepted Sulfreen process (Michel, 1977) was introduced as an additional cleanup stage during the 1960's. It can greatly decrease the sulfur losses from H_2S and SO_2 but does not affect CS_2 and COS removal. The high performance titania-based catalyst, CRS 31, created by Rhone-Poulenc (Dupin and Vermeersh, 1982) effectively reduces CS_2 and COS , but costs considerably more than alumina catalysts. The installation of a mullite catalyst in a Claus furnace for removal of CS_2 and COS was suggested (Luinstra and d'Haene, 1989), but it is expected to be difficult to overcome the problem of instability of this catalyst under extremely high Claus furnace temperatures.

Figure 3.1 Modified Claus Process Technology (Current)



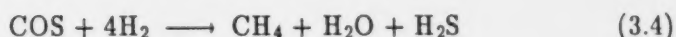
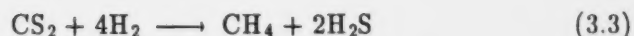
The main reactions for the removal of CS₂ and COS proposed in the literature (Grancher, 1978; George, 1974; Chuang, Dalla Lana and Liu, 1973) are:

Hydrolysis:



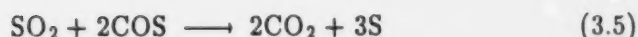
alumina catalyst, 200°C – 300°C

Reduction



Co–Mo/Al₂O₃, 350°C – 400°C

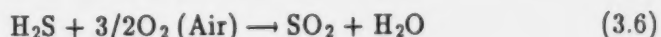
Redox



Co–Mo/Al₂O₃, 350°C – 400°C

For these three methods, the involvement of an expensive Co–Mo–Al₂O₃ catalyst combined with the comparatively high temperature needed for the reduction reactions (3.3) and (3.4) and redox reaction (3.5) limits their practical application. On the other hand, reactions (3.1) and (3.2) possess several advantages.

H₂O is directly produced from the modified Claus reactions,

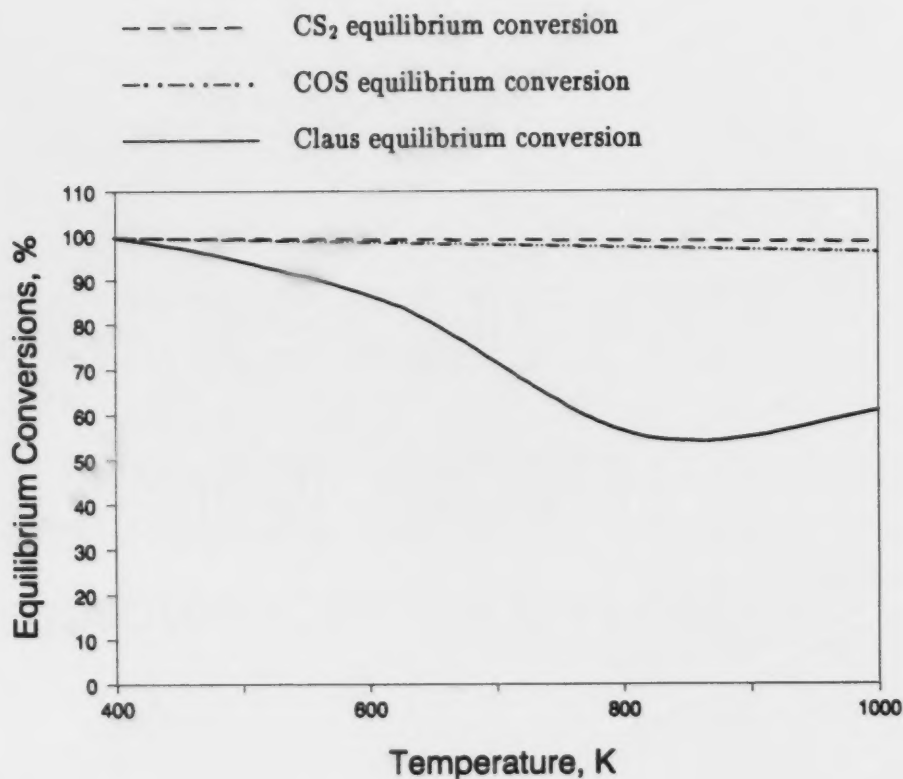


and is present in large amounts. The reaction temperature required for the hydrolysis reaction using an "inexpensive" alumina catalyst is also within the temperature range of Claus converters (200°C to 350°C). Surprisingly, no systematic investigation of this topic is apparent in the literature even though it possesses advantages. Moreover, our calculations of the thermodynamic

equilibrium conversions for the reversible hydrolysis reactions of both CS_2 and COS and for the Claus reaction, shown in Figure 3.2, indicate that the equilibrium conversions for the reactions, (3.1) and (3.2), exceed 98% over the reaction temperature range irrespective of the equilibrium conversion limitation for the Claus reaction, (3.6) and (3.7). The hydrolysis reactions, (3.1) and (3.2), are thermodynamically quite favorable.

However, irrespective of the thermodynamic equilibrium predictions,

Figure 3.2 Thermodynamic Equilibrium Conversion



traditional alumina catalysts in Claus plants often fail to ensure equilibrium conversion levels for the hydrolysis reactions. The design of an improved alumina-based Claus catalyst for the effective removal of CS_2 and COS is still a desirable objective. Although titania-based catalysts have been found to be more active than alumina catalysts for hydrolysis reactions, no results have been published to date pursuing the reason for the different hydrolysis activities of the two types of catalysts. It was experimentally observed that the hydrolysis reactions are relatively fast for COS but considerably slower for CS_2 (Akimoto and Dalla Lana, 1980, 1979). In the work reported herein, the slower CS_2 hydrolysis reaction will be used as the model reaction to test and compare activities of several available commercial Claus catalysts.

3.2 EXPERIMENTAL DETAILS

3.2.1 Materials

In all experiments, high purity nitrogen (99.99%) purchased from Linde was used as the diluent for the reaction gases. Carbon disulfide (>99.9 % purity) was obtained from BDH chemicals.

Three types of industrial Claus catalysts, bauxite, alumina and titania, were examined. Kaiser 201 (alumina) and CRS 31 (titania) are most commonly used in Alberta gas processing plants. An old sample of activated bauxite (Porocel) from Engelhard and a less commonly used promoted alumina, Kaiser 501, were also examined. Their physical details are listed in Tables 3.1 and 3.2. The surface area and pore distribution of these catalysts were obtained using an OMNISORP 360 (N_2 adsorption) as shown in Table 3.3. The TGA analysis was made using a Perkin-Elmer Model TGS-2 thermogravimetric analyzer.

3.2.2 Equipment

The schematic diagram of the experimental apparatus was described in Chapter 2, Figure 2.1. A Berty reactor was used to measure the steady-state rate of CS₂ hydrolysis at operating temperatures ranging from 170°C to 350°C. The feed compounds, CS₂ and H₂O, were introduced by saturating two streams of high purity nitrogen with either H₂O or CS₂. The well-mixed combined feed stream, after passing the sampling valve for feed analysis, was preheated before entering the Berty reactor. The exit stream from the Berty reactor was also sampled and then analyzed by online gas chromatography and then vented. The concentration of H₂O in the feed was regulated by choosing a saturation temperature to give the

Table 3.1 Catalyst and Physical Nature

Catalyst	Shape	Size (mm)
Kaiser 201	Sphere	4
Kaiser 501	Sphere	3
Activated Bauxite	Granular	1–1.4
CRS 31	Extrudate	3.5–4

Table 3.2 Specific Surface Areas and Average Physical Properties

Catalyst	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Radius (nm)	Particle Density (g/cm ³)	Porosity
Kaiser 201	296.1	0.418	3.00	1.58	0.6604
Bauxite	217.3	0.142	3.04	—	—
CRS 31	85.7	0.263	6.82	1.47	0.3866

Table 3.3 Pore Size and Surface Area Distributions

Catalyst	Pore Radius (nm)	Pore Volume (cm ³ /g)	Pore size Distribution (%)	Surface Area Distribution (%)
Kaiser 201	>20	0	0	0
	20-10	0.01075	2.57	0.38
	10-5	0.02913	6.97	2.06
	5-4	0.01886	4.51	2.22
	4-3	0.0485	11.60	7.34
	3-2	0.155	37.08	32.86
	2-1	0.156	37.32	55.12
CRS 31	>20	0	0	0
	20-10	0.03390	12.89	4.67
	10-5	0.22500	43.73	31.66
	5-4	0.05277	20.06	24.21
	4-3	0.03761	14.30	22.19
	3-2	0.02091	7.95	17.27
	2-1	0.00304	1.16	4.18

desired water vapor pressure in a specified flowrate of the carrier gas (nitrogen). The desired water vapor pressure was obtained by regulating a water bath at the desired temperature using a Thermomix 1420 regulator. The nitrogen flowrate was controlled with a digital mass flowmeter. The CS₂ concentration in the feed was adjusted using the same method used for obtaining the desired water concentration, but the CS₂ vapor pressure was controlled by saturating the N₂ in a refrigerated bath. Through proper setting of the water bath temperature, refrigerated bath temperature and both nitrogen flowrates, the feed compositions could be adjusted over a broad range. In many experiments, standard 2 mol% H₂O and 1 mol% CS₂ concentration were used to evaluate the catalysts. The system pressure was stabilized near atmospheric pressure by a Foxboro pressure controller. Testing of the experimental equipment system in the absence of a

catalyst showed no catalytic activity for the CS₂ hydrolysis.

3.2.3 Gas Analysis

The gaseous feed and effluent from the reactor were analyzed by gas chromatography. A 3 m x 0.03 m Porapak QS column was used with a helium flowrate of 35 NTP mL/min. The separation of the product constituents involved two GC oven temperatures of 60°C and 130°C. Figure 2.3 in Chapter 2 shows the separation chromatogram. The low boiling-point components, CO₂, COS and H₂S, were analyzed at 60°C and the high boiling-point compounds, CS₂ and H₂O, were analyzed at 130°C. The sampling valves were housed in an insulated box maintained at 100°C.

3.2.4 Experimental Procedure

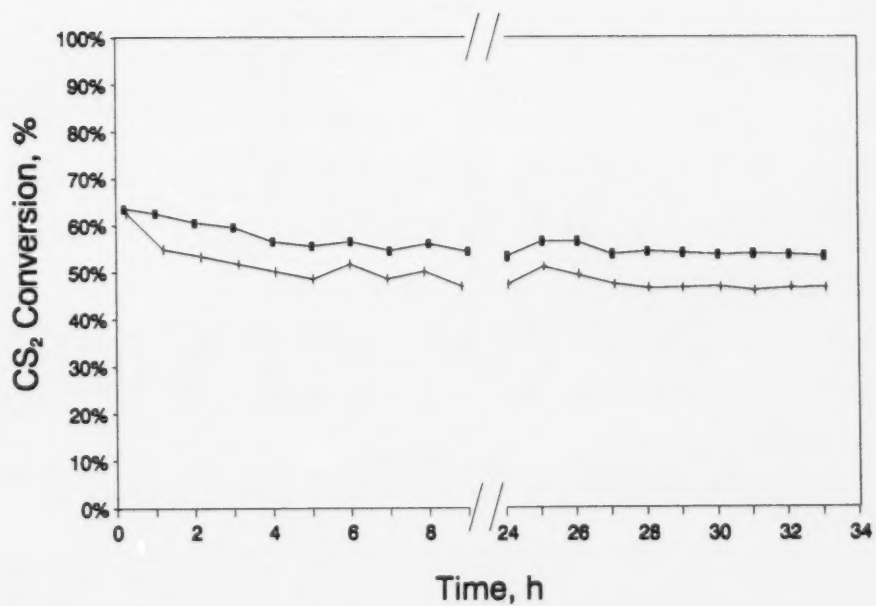
For each batch of 2 g catalyst loaded in the Berty reactor, the temperature was raised to the desired testing temperature and held there for 24 h to ensure a uniform temperature inside the Berty reactor (monitored by four thermocouples: one for catalyst bed temperature, three for reactor wall temperatures at different locations). A slow stream of dry nitrogen was passed through the catalyst bed during this period. The catalyst surface was then exposed to a feed stream of 2 mol% H₂O, 1 mol% CS₂ and 97 mol% N₂. The reaction conditions were continued for 5 h to ensure steady-state of the reaction (as suggested by the stability testing, Figure 3.3) before the experimental data were collected. The composition of the exit stream from the Berty reactor was determined hourly and a total of five samples was averaged for each experimental run. This approach enabled the measurement of global rates of reaction, i.e., the performance of the catalyst as supplied by the manufacturer.

Figure 3.3 Stability of Catalysts

Temperature = 300°C, Pressure = 150 kPa, Feed Flowrate = 0.03 m³/h

Feed Compositions, mol %: CS₂ = 1.09, H₂O = 2.01, N₂ = 96.7

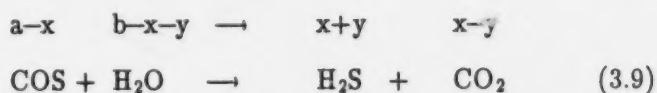
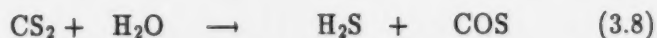
+ Alumina Kaiser 201, ■ Titania



3.3 RESULTS AND DISCUSSION

3.3.1 Reliability Check of the Experimental Data

For the comparison of catalytic activity for CS₂ hydrolysis, the stability period of the catalysts was tested on a representative industrial alumina catalyst, Kaiser 201 and a titania-based catalyst, CRS 31. Figure 3.3 shows that the catalytic activity of the catalysts decreases slightly with time, but changes negligibly after 5 h. The reliability of the GC data was checked through stoichiometric calculations based upon the two consecutive reactions (3.8) and (3.9),



where *a* and *b* are the inlet CS₂ and H₂O concentrations (mol %), respectively, *x* is the reacted CS₂ mol % in reaction (3.8) and *y* is the CO₂ mol % produced via reaction (3.9). Since the net change in moles from reactions was zero, "mol %" units could be used in the stoichiometric calculations. At steady state, the measured [CO₂] and [H₂O] were used to calculate *x* and *y*, from which [H₂S], [CS₂] and [COS] can be estimated. The comparison of calculated values with experimental values are shown in Figure 3.4. With elapse of time, the difference between experimental and calculated values gradually converges to a very small value after 5 h. The catalytic unsteady-state exhibited in the first 5 h may be attributed to the deposition of carbon on the catalyst, which could be observed on the catalyst after the experiment. The experimental data collected after 5 hours

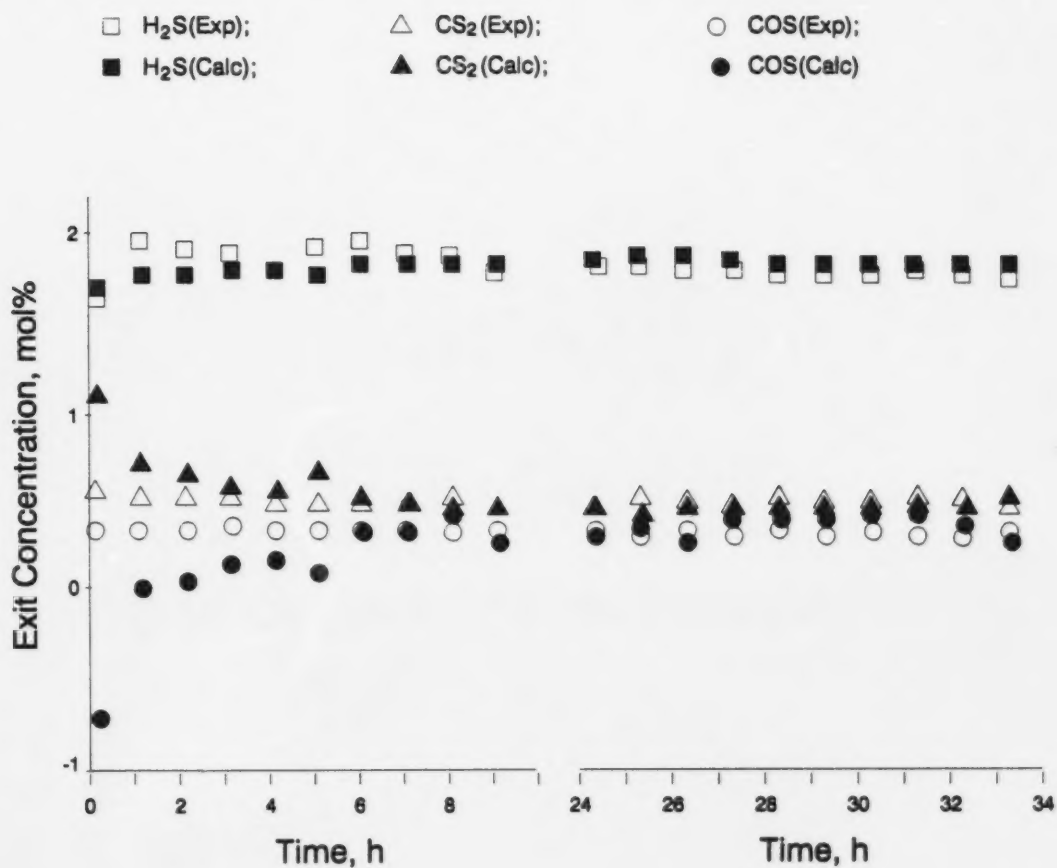
Figure 3.4 Reliability Check of Analytical Data

Testing Condition:

Reaction Temperature = 300°C, Pressure = 150 kPa

Feed Flowrate = 0.03 m³/h, Catalyst Weight = 2.0 g

Feed Composition, mol %: CS₂ = 1.09, H₂O = 2.01, N₂ = 96.9



were believed to be from the period of steady state catalytic reaction.

3.3.2 Catalyst Performance

The steady-state CS_2 catalytic hydrolysis rates (based on the unit weight of the catalyst) are presented in Figure 3.5. At the standardized condition of 300°C , 1.09 mol % inlet CS_2 and 2.05 mol % inlet H_2O concentration, the titania CRS 31, appears to be the most active among the three catalysts tested. Figure 3.5 shows that the largest rate of disappearance of CS_2 coincided with the lowest rate of appearance of COS. Since the intermediate COS produced from reaction (3.8) could disappear through reaction (3.9), the more active catalyst could catalyze reaction (3.9) faster than reaction (3.8) and results in the lower COS concentration and rate of appearance of COS. The COS rate of appearance in the Berty reactor with $\text{CS}_2/\text{H}_2\text{O}/\text{N}_2$ feed was calculated by using equation (3.10),

$$r_{\text{COS}} = \frac{(X_{\text{COS}})_{\text{out}} - (X_{\text{COS}})_{\text{in}}}{W} \times \frac{F_t \cdot P_t}{R \cdot T}, \text{ mol/g} \cdot \text{h} \quad (3.10)$$

Since the intermediate COS produced from reaction (3.8) can disappear through reaction (3.9), the more active catalyst can catalyze reaction (3.9) faster than reaction (3.8) and result in the lower COS concentration. Therefore, the smaller the concentration of COS in the effluent, the smaller the COS appearance rate will be.

Figure 3.6 shows that for titania and alumina catalysts from 170°C to 350°C , the change in CS_2 hydrolysis rate with temperature on titania was larger than on the alumina catalysts. Below 230°C , alumina (Kaiser 201) and titania (CRS 31) exhibit little difference in the rate of hydrolysis of CS_2 . Above 230°C ,

Figure 3.5 Comparison of Catalyst Performance at Standardized Conditions

Testing Condition:

Reaction Temperature, 300°C, Pressure = 150 kPa

Feed Flowrate = 0.03 m³/h

Feed Composition, mol %: CS₂ = 1.09, H₂O = 2.01, N₂ = 96.9

Catalyst Weight = 2.0 g

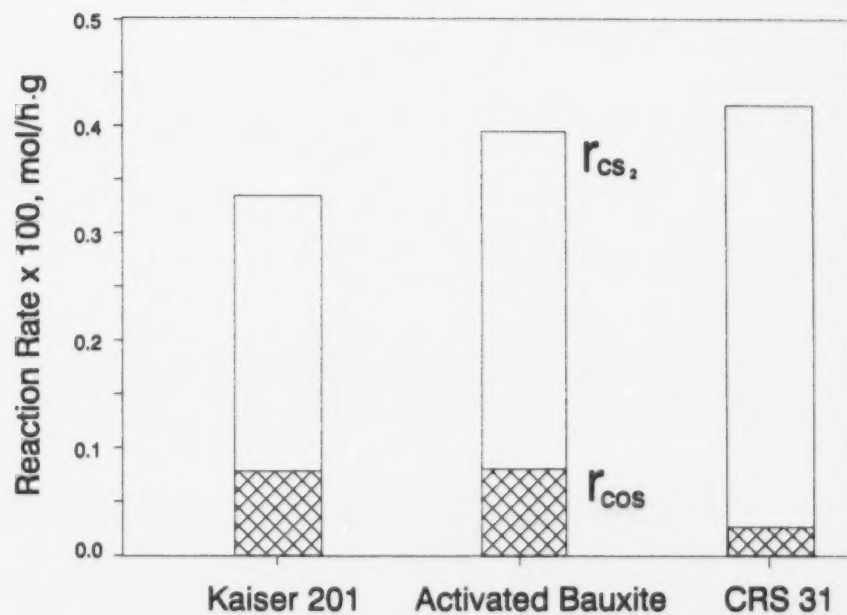


Figure 3.6 Comparison of Catalyst Performance at Different Temperatures

Test Condition:

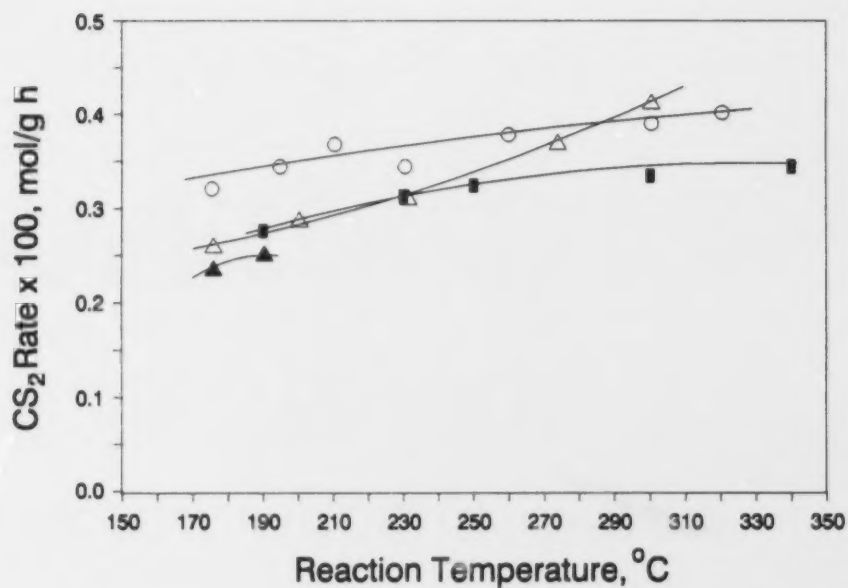
Reaction Temperature = 230 to 340°C, Pressure = 150 kPa

Feed Flowrate = 0.03 m³/h

Feed Composition, mol %: CS₂ = 1.09, H₂O = 2.01, N₂ = 96.9

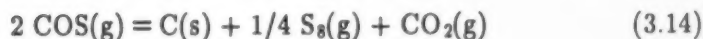
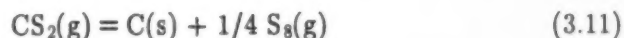
Catalyst Weight = 2.0 g

△ CRS 31; ○ Activated Bauxite; ▲ Kaiser 501; ■ Kaiser 201



the CS₂ hydrolysis rate on the titania CRS 31 increases more rapidly than on the alumina. At the same test conditions, the activated bauxite appears to be the most effective of the three catalysts tested for the hydrolysis of CS₂ up to 290°C. Above 290°C, titania CRS 31 appears to be the most active. The bauxite and Kaiser 201 exhibit parallel behavior (expected since both are alumina-based catalysts) whereas the CRS 31 shows substantially more temperature-sensitivity for CS₂ hydrolysis.

For the second alumina (Kaiser 501), only two experimental points were obtained since, above 200°C, the exit passage of the equipment became blocked by deposition of sulfur produced during the reaction. Visual inspection clearly revealed a layer of yellow sulfur covering the surface of the catalyst. Nemeth and Gati (1990) observed similar phenomenon in their research of carbonyl sulphide synthesis from carbon disulfide and carbon dioxide on alumina catalysts. They reported that the CS₂ decomposition reactions (3.11) to (3.16),



are possible thermodynamically. The alumina Kaiser 501 appears to be a catalyst which favors such cracking reactions.

Since both alumina and titania are hydrophilic materials, their catalytic behavior for the hydrolysis reactions is expected to be related to adsorbed water on

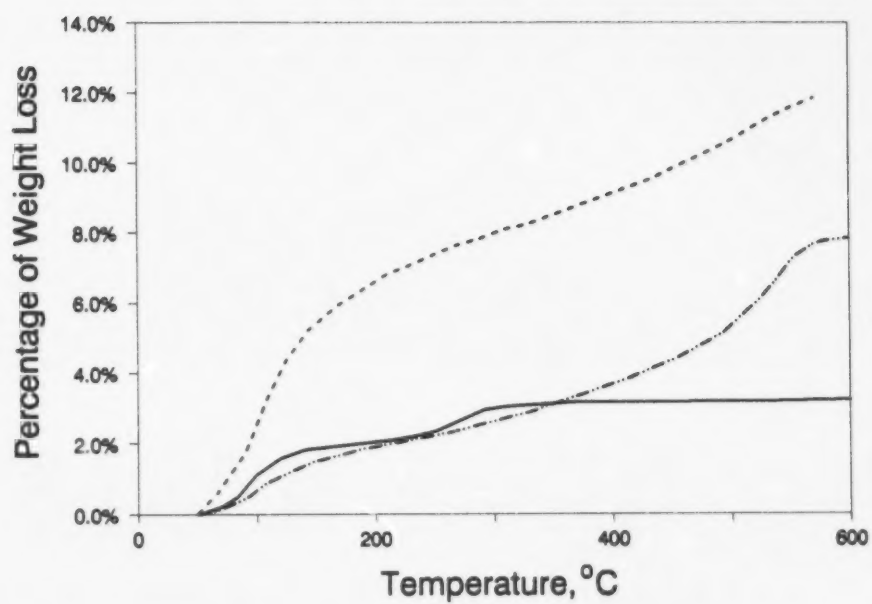
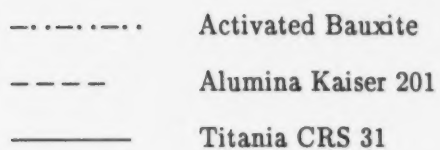
the surface. Stronger water adsorption on alumina Kaiser 201 and activated bauxite as compared to water adsorption on titania CRS was confirmed by thermogravimetric analysis. Figure 3.7 presents the TGA graph of alumina Kaiser 201, activated bauxite and titania CRS 31 with temperature scanning from 50°C to 550°C for the alumina-based catalysts and 50°C to 500°C for titania-based CRS 31. Two types of weight loss curve were observed on these catalysts. For CRS 31, the two-stage loss curve suggests the removal of surface (adsorbed) water preceded by the removal of the more tightly bound "crystal" water. The first stage weight loss was completed at 140°C and then the more tightly bound water was released starting at 220°C up to about 300°C. The total water loss from CRS 31 comprised 3% of the catalyst weight. In contrast, the alumina catalysts, Kaiser 201 and activated bauxite, exhibited continuing water losses up to the maximum TGA temperature, 550°C. The weight losses on Kaiser 201 and activated bauxite were 12 % and 8 %, respectively, with retention of additional water being likely.

Figure 3.6 shows that the catalytic activity of CRS 31 for CS₂ hydrolysis began to exceed that of Kaiser 201 at 230°C, and that of bauxite at 290°C. TGA shows that water removal by heating was completed near 300°C for CRS 31 but not for alumina or bauxite. These nearly co-incident effects suggest that excessive adsorbed water is detrimental to CS₂ hydrolysis. The CS₂ molecule more easily interacts with active sites on the surface of CRS 31 than on Kaiser 201 above 230°C.

3.3.3 Pore Structure of the Catalysts

As suggested earlier, the hydrolysis rate appears to be strongly affected by the surface water on the catalysts, more so on a strongly hydrophilic catalyst like alumina than on a less hydrophilic catalyst like titania. Water vapor may also

Figure 3.7 Thermogravimetric Analysis of Water Loss



lower catalytic activity by blocking micropores through capillary condensation. Figure 3.8 shows the pore size distributions for Kaiser 201, CRS 31 and the activated bauxite.

The limiting radii of cylindrical pores were calculated using the Kelvin equation at the maximum water vapour concentration (30 mol %) typically encountered in the first stage catalytic converters in modified Claus plants. Figure 3.9 shows the limiting capillary radii as a function of temperature. When these limiting values are compared to the pore size distributions of the catalysts, only micropores with average pore radii of 0.34 nm or less are affected by capillary condensation of water. The contribution to the total surface area of the catalysts by these 0.34 nm or smaller micropores is negligible. This means that the difference in catalytic behavior between alumina and titania catalysts could not be attributed to capillary condensation of water vapor.

However, similar estimates of capillary condensation of sulfur vapor in the first Claus converter for the case of a modified Claus plant with 60 mol % H_2S acid gas feed, 80.0% conversion to elemental sulfur, and with equilibrium polysulfur distributions in the gas phase are shown by the black bar in Figure 3.9. In this case, important micropore blockage occurs in the pore range below 2.2 nm. This inaccessible area covers a large part of the internal pore distribution range possessed by the alumina and activated bauxite catalysts. The pore-size distribution in Table 3.3 shows that over 55 % of the surface area arises in pores below 2 nm in alumina compared with 4 % of the surface area below 2 nm in titania. At the same temperature, a much larger volume of pores in the alumina catalysts may be filled with condensed sulfur than in the titania catalyst. The result not only may change the range of available pore sizes but can eliminate much of the internal surface of the catalyst.

Figure 3.8 Pore Size Distribution

..... Alumina Kaiser 201
----- Activated Bauxite
———— Titania CRS 31

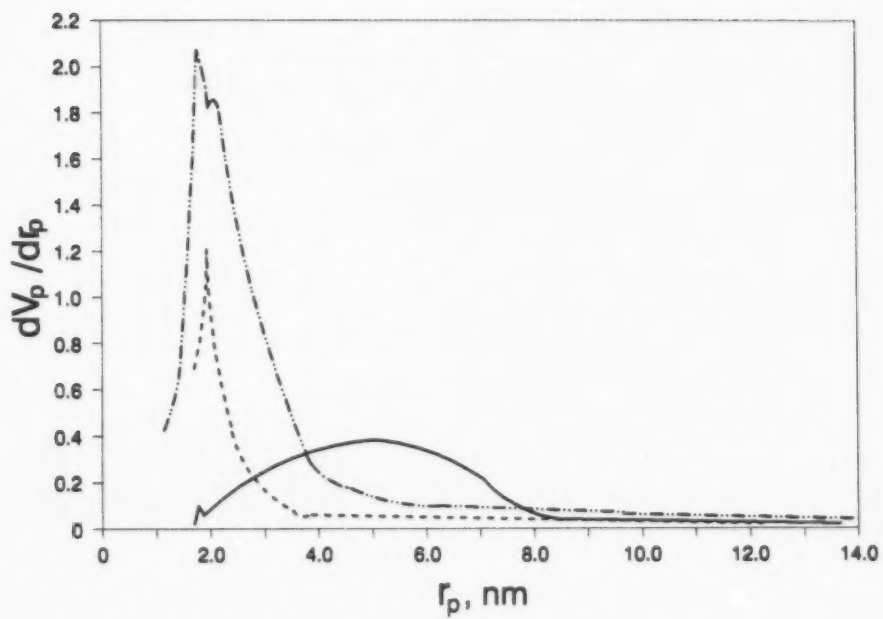
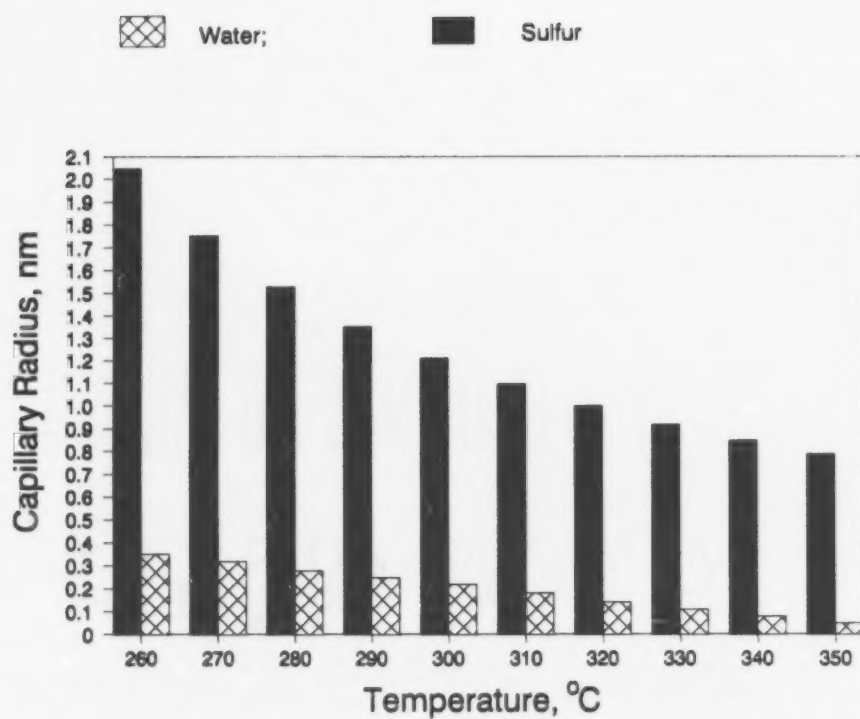


Figure 3.9 Capillary Condensation at Different Temperatures



In practice, higher reaction temperatures are required for alumina to hydrolyze both CS_2 and COS in commercial Claus process reactors. If capillary condensation of sulfur inhibits the hydrolysis rate by blocking access to catalyst pore surface, then raising the reaction temperature would reduce the influence of capillary condensation of sulfur. The hydrolysis reactions, in principle, exhibit favorable kinetics at Claus converter temperatures but excessive adsorption of water vapor alone, with this reduction in accessible surface area, suppresses the reaction rates.

Table 3.2 summarizes the physical parameters of alumina Kaiser 201 and titania CRS 31 from pore-size distribution measurements. Table 3.3 presents both pore volume and surface area distributions. The internal surface distribution percentage, Y_{s_i} , for each pore size range is calculated on the assumption of a cylindrical pore model according to equation (3.17),

$$Y_{s_i} = 2V_{gi}/(r_i \times 10^{-7} \Sigma S_{gi} \cdot 10^4) \quad (3.17)$$

For Kaiser 201, Figure 3.9 shows that at 300°C , the micropores from roughly 1 to 2 nm could be filled by capillary condensed sulfur; thus, 37 % of the total pore volume and 55 % of the surface area was blocked. Comparatively, CRS 31, shows only roughly 1 % reduction in pore volume and 4 % reduction in surface area. Because the pore size distribution of the alumina catalyst overlaps the range favoring sulfur capillary condensation, one may expect some lowering of both Claus conversion activity and CS_2 hydrolysis activity for the alumina catalyst relative to CRS 31.

3.4 CONCLUSIONS

1. The hydrolysis of CS_2 over alumina- and titania-based catalysts was investigated at isothermal test conditions ranging from 170°C to 330°C and reactant concentrations of 1 mol % CS_2 and 2 mol % H_2O . The two alumina-based catalysts (Kaiser 201 and activated bauxite) exhibited parallel temperature behavior with the bauxite exhibiting the highest activity of the three catalysts tested up to 290°C. The titania catalyst (CRS 31) showed the greatest temperature influence on catalyst activity and displayed the highest activity above 290°C. The strong hydrophilic character of alumina and bauxite suppresses their catalytic activity over the entire temperature range tested whereas the titania catalyst is essentially hydrophobic above 290°C.

2. The possibility of capillary condensation of water within the catalyst pores being partially responsible for the reduction in catalytic activity was examined. For the pore size distribution (PSD) of both CRS 31 and Kaiser 201 exposed to water vapor content as high as 30 % (in a Claus catalytic converter) at temperatures ranging from 260°C to 350°C, negligible reduction in surface area was expected since only slight capillary condensation was predicted.

3. The possibility of capillary condensation of sulfur vapor within the catalyst pores was also examined at the same conditions cited under 2. Major blockage of pore volume was predicted for Kaiser 201 because of its narrow and smaller PSD whereas the CRS 31 was not severely affected. The practical experience in modified Claus plants in which alumina catalysts are observed to hydrolyze CS_2 and COS only at the elevated temperatures found in the first stage converter may be attributed to this means of preventing such condensation of sulfur vapor.

4. Operation of cold-bed Claus converters (temperature $< 260^{\circ}\text{C}$) using alumina catalysts is likely to be ineffective for CS_2 hydrolysis because of the major reduction in accessible catalyst surface and the competition with water for adsorption sites. Similar but less severe effects may be anticipated for CRS 31.

3.5 NOMENCLATURE

a, b	=	inlet CS_2 and H_2O concentrations, mol %
C_{CS_2}	=	CS_2 concentration, mol %
$C_{\text{H}_2\text{O}}$	=	H_2O concentration, mol %
C_{COS}	=	COS concentration, mol %
F_t	=	total feed gas flowrate, m^3/h
P_t	=	pressure, kPa
R	=	gas constant, $\text{kJ}/(\text{mol} \cdot \text{K})$
r_{COS}	=	COS hydrolysis rate, $\text{mol}/(\text{g} \cdot \text{h})$
r_{CS_2}	=	CS_2 hydrolysis rate, $\text{mol}/(\text{g} \cdot \text{h})$
r_i	=	pore radius, i th size, nm
S_{gi}	=	internal surface area, i th pore size, m^2/g
T	=	reaction temperature, K
V	=	particle volume, m^3/g
V_{gi}	=	specific pore volume, i th pore size, cm^3/g
W	=	catalyst weight, g
Y_{si}	=	percentage of total internal surface area, i th pore size

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CHAPTER 4

KINETIC MODELLING OF THE HYDROLYSIS OF CARBONYL SULFIDE CATALYZED BY TITANIA OR ALUMINA

4.1 INTRODUCTION

In Chapter 3, the relative performances of both titania-based and alumina-based catalysts for the catalytic hydrolysis of CS_2 were investigated using the following reactions:



It was shown that above 290°C , the titania based catalyst appeared to be an increasingly better hydrolysis catalyst for the above reactions. It was also shown by thermogravimetric measurement that alumina's inherent hydrophilic character retained large amounts of adsorbed water even at the highest temperature (up to 500°C) tested, unlike titania. An attempt was therefore made to study the water effect on the two types of catalysts by establishing kinetic rate functions for both catalysts.

A few kinetic models for the hydrolysis of COS were proposed in the earlier works (Fiedorow et al., 1984; Akimoto and Dalla Lana, 1979; Kerr et al., 1976; Zhang and Guo, 1988). But all the previous experimental work on this subject was done at or below 200°C which is less meaningful when the practical operating temperature ranges of the first Claus converter in the modified Claus process are considered. The first Claus converter normally operates around 300°C and was suggested to be the best location for the elimination of COS and CS_2 by the hydrolysis reaction (Grancher, 1978). During the earlier experimental searches of rate equations for the hydrolysis of COS, the equations were obtained either by using linear regression for a first order COS concentration when the water concentration was kept at a higher level (above 4 %) or by nonlinear regression when a more complicated effect of water was to be considered in the rate equation. In the former case, the rate equation with pseudo-first order COS concentration

concealed the water effect on the hydrolysis rate, which was different on different catalysts and in different temperature ranges. When the water effect was expressed in a rate equation such as the Eley-Rideal model or the Langmuir-Hinshelwood type of function, nonlinear regression was necessary to establish the correct rate function. A least square estimator of a parameter in a nonlinear model, unlike that of a linear model, has essentially unknown properties when finite sample sizes are used. Thus, the simple use of statistical tests such as an F test or a student t test, which are established on the basis of linear theory, for the reliability check of a nonlinear model or its estimated parameters could lead to a wrong conclusion. Bates and Watts (1980) developed a "curvature measure" method to quantify a nonlinear model by a number called a degree of nonlinearity. For a certain data/model set combination, the nonlinearity of the model could be reduced by reparameterization. If the quantified degree of nonlinearity was less than a critical value, $1/2(F)^{0.5}$, the nonlinear problem for the data/model set combination could be treated as a linear problem. Therefore, a statistical model-fitting and goodness test such as the F test could then be used to check the validity of the "linearized" nonlinear model. It could be expected that the convergence of model regression through numerical iterations would become unique when the nonlinear model approaches linear properties.

In this research, the kinetic measurements for the reaction of COS hydrolysis on both titania-based CRS 31 and alumina-based Kaiser 201 were approached under controlled conditions in a Berty type laboratory reactor. The experimental reaction temperature was set from 270°C to 330°C by simulating the conditions in the first Claus converter in the modified Claus process.

In the data/model screening work to be described herein, several "mechanism-based" rate functions exhibiting water inhibition effects were tested.

Bates and Watts' "curvature measure" (1980) was employed in combination with a simulation study (Ratkowsky, 1983) and Box's bias calculation (Box, 1971) of the model parameters (estimated from the nonlinear regression analysis). Kinetic parameters for both titania CRS 31 and Kaiser 201 rate equations were obtained by regression.

4.2 EXPERIMENTAL

4.2.1 Methods

COS hydrolysis rates were measured using a Berty type reactor over the temperature range, 270 to 330°C. At each reaction temperature tested, the total gas flow ($\text{COS} + \text{H}_2\text{O} + \text{N}_2$) was maintained at $3 \times 10^{-2} \text{ m}^3/\text{h}$ and 150 kPa. To study the pressure dependence, the partial pressure of COS and H_2O were regulated as follows: the particular flow rates of COS (5 % COS/ N_2 , Matheson) and N_2 (high purity, 99.99 %, Matheson) were maintained with the help of mass flow controllers calibrated for both gases. Then, the N_2 gas stream was passed through a thermostatted bubbler holding deionized water. At each fixed value of COS partial pressure from 0.75 to 3 kPa (0.5 to 2.0 mol %), the H_2O partial pressure was varied between 3 and 18 kPa (2 to 12 mol %).

Prior to the measurement of the rate of reaction, the catalysts were crushed to test the effect of particle size on internal diffusion. Figure 4.1 shows that the reaction is free of internal diffusion limitation when particle sizes are within the ranges, -25+30 mesh, or smaller. In each experiment, 2 g of catalyst were used. The reaction mixture was preheated before entering the Berty reactor. The reaction rate in the absence of catalyst was immeasurably slow. A detailed description of the equipment and the feed-product analysis was presented in Chapter 2.

Figure 4.1 Effect of Catalyst Particle Size on COS Hydrolysis

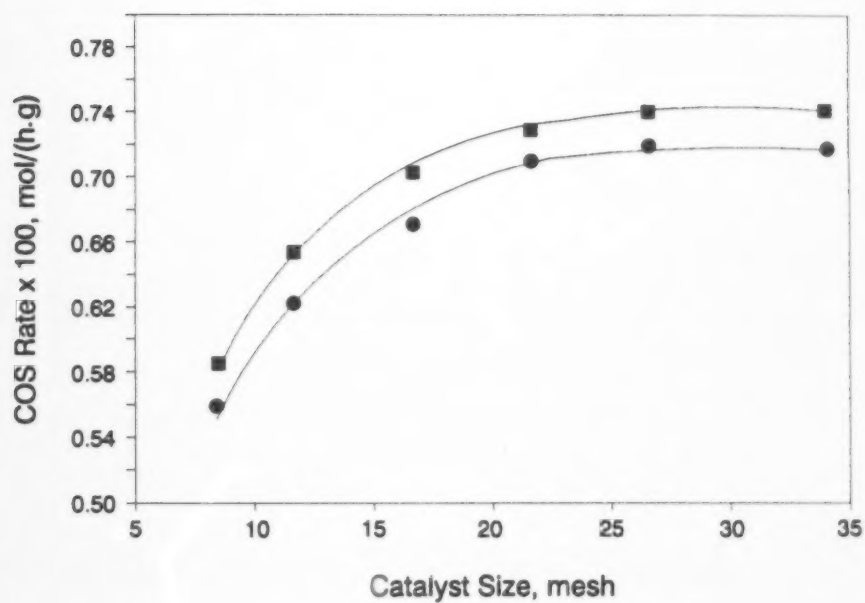
Test Conditions:

Temperature = 300°C, Pressure = 150 kPa

Feed Flowrate = 0.03 m³/h, Catalyst Weight = 2 g

Feed Composition, mol %: COS = 1.00, H₂O = 2.0, N₂ = 97

● Kaiser 201 ■ CRS 31



4.2.2 Catalysts

The catalysts under study were as follows:

CRS 31: A titania-based catalyst developed by Rhone-Poulenc and SNEA with the following characteristics,

Shape	Extrudates
Diameter	3.5 to 4 mm
Bulk Density	0.95 to 1.05 g/cm ³
Specific Surface Area	100 to 140 m ² /g
TiO ₂ Content	≥ 85 percent

Kaiser 201: An alumina-based catalyst with the following specifications,

Shape	Spherical
Specific Surface Area	380 m ² /G
Percent of: Al ₂ O ₃	93.60
SiO ₂	0.20
Fe ₂ O ₃	0.20
TiO ₂	0.02
Na ₂ O	0.30

The catalysts were supplied in the form of spherical pellets (Kaiser 201) or extrudates (CRS 31). The catalysts were crushed and sieved, the -25+30 mesh fractions being used for the measurement of intrinsic rates of the hydrolysis of COS.

4.2.3 Pretreatment

Prior to the kinetics experiments, the catalysts were kept under a high purity nitrogen flow, also at 300°C, for 2 h until the temperature of the reactor, monitored by three thermocouples, became constant. Then, the nitrogen flow was replaced by the feed gas flow (COS + H₂O + N₂). The reaction state was

maintained for at least 5 h to ensure that the catalyst activity was at steady-state. The test for catalyst life and steady-state approaching time, and the reliability check of the GC analytical data have been described in Chapters 2 and 3.

4.3 RESULTS AND DISCUSSION

4.3.1 Kinetic Study on Alumina Kaiser 201 and Titania CRS 31

In the flow Berty reactor experiments, the catalytic activity was sufficiently stable after 5 h under feed flow to generate reliable kinetic parameters.

The reaction rate was calculated using equation (4.3) for a Berty type of reactor which operated at ideal CSTR condition.

$$-r_{\text{cos}} = \frac{(X_{\text{cos}})_{\text{in}} - (X_{\text{cos}})_{\text{out}}}{W} \times \frac{F_t \cdot P_t}{R \cdot T}, \text{ mol/h} \cdot \text{g} \quad (4.3)$$

Figures 4.2 and 4.3 show the changes in the COS hydrolysis rate with varying H₂O partial pressure at a fixed inlet COS level for both catalysts, CRS 31 and Kaiser 201. As shown in the Figures, the hydrolysis rate of COS approached a constant value with increasing water concentration for both CRS 31 and Kaiser 201 at each temperature tested (270°C, 300°C and 330°C). But the hydrolysis rate appeared to increase with COS concentration. Generally, the intrinsic hydrolysis rates on CRS 31 are higher than on Kaiser 201 but the difference is not as great as those reported on severely aged catalysts or tested in the Claus process (Engelhard, 1991). At the design conditions, the test involved COS hydrolysis alone on fresh catalyst; whereas, at Claus plant conditions, both capillary condensation of sulfur and sulfation problems may be encountered. The main

Figure 4.2 Intrinsic Rate of COS Hydrolysis on Alumina (Kaiser 201)

Test Conditions:

Temperature = 270 to 330°C, Pressure = 150 kPa,

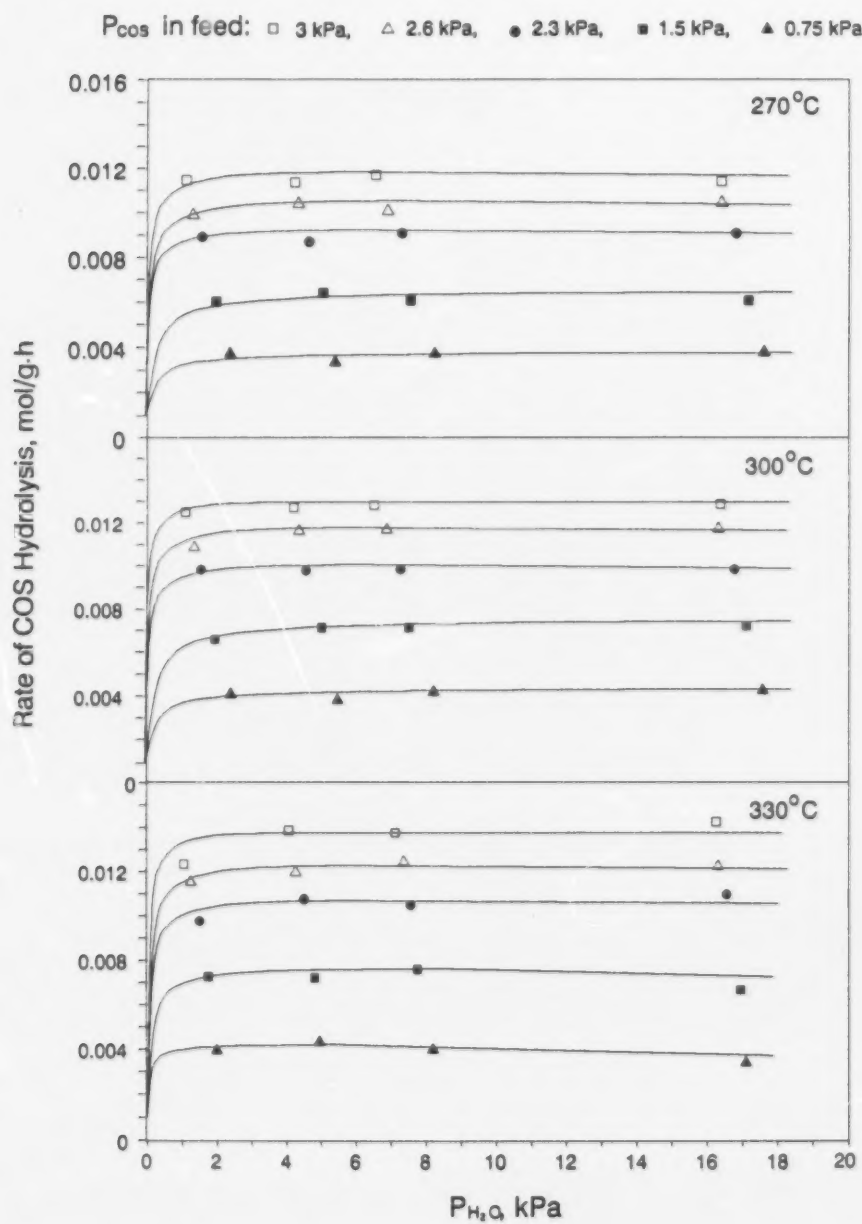
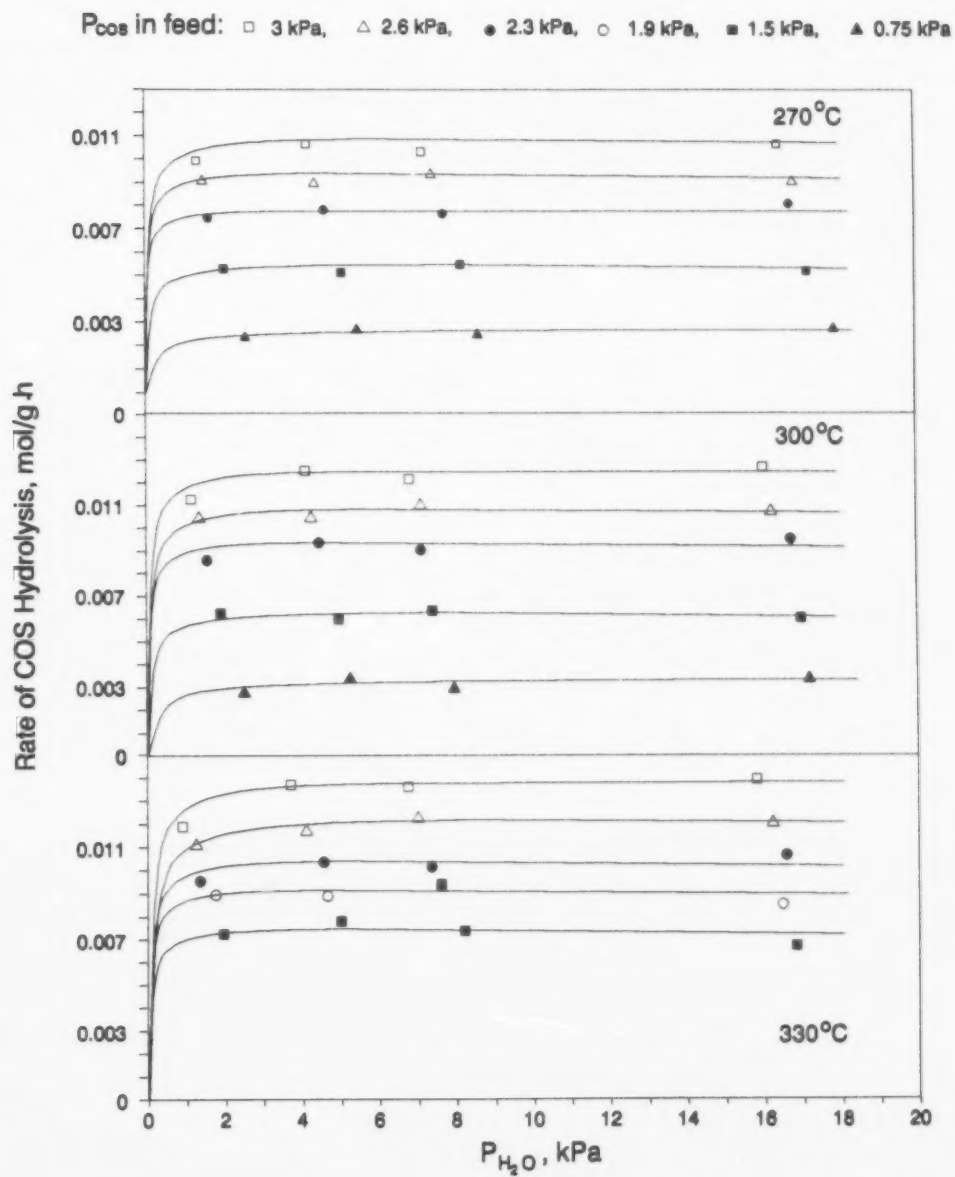
Feed Flowrate = 0.03 m³/h, Catalyst Weight = 2.02 g.

Figure 4.3 Intrinsic Rate of COS Hydrolysis on Titania (CRS 31)

Test Conditions:

Temperature = 270 to 330°C, Pressure = 150 kPa,

Feed Flowrate = 0.03 m³/h, Catalyst Weight = 2.02 g

influences on the intrinsic rate of COS hydrolysis in these experiments could be attributed to water vapor in the system and COS concentrations. In the previous thermogravimetric study (Chapter 3), the water contained in CRS 31 could be completely removed below 300°C, but not in Kaiser 201, which retained a large amount of water in the range of temperatures tested in the following kinetics study. The less hydrophilic CRS 31 showed more active hydrolysis activity whereas the more hydrophilic Kaiser 201 exhibited less activity. This implies that water, though a necessary reactant for the hydrolysis, may play an inhibiting effect when retained on the catalyst surface. In the following discussion, several rate functions which exhibit water inhibition effect were employed in the search for the best-fitting rate function.

4.3.2 Rate Function

By looking at the hydrolysis characteristics in Figures 4.2 and 4.3, the following four models functions were postulated for the irreversible hydrolysis of COS:

Eley-Rideal Model (ER)

$$-r_{\text{COS}} = \frac{k_2 K_w P_{\text{COS}} P_{\text{H}_2\text{O}}}{1 + K_w P_{\text{H}_2\text{O}}} \quad (4.4)$$

Modified Eley-Rideal Model (MER)

$$-r_{\text{COS}} = \frac{k_2 K_w P_{\text{COS}} P_{\text{H}_2\text{O}}}{(1 + K_w P_{\text{H}_2\text{O}})^n} \quad (4.5)$$

where the value of n emphasizes the strength of the water inhibition effect.

Langmuir-Hinshelwood Model 1 (LH1)

$$-r_{\text{COS}} = \frac{k_2 K_{\text{C}_2} K_{\text{w}_2} P_{\text{COS}} P_{\text{H}_2\text{O}}}{1 + K_{\text{C}_2} P_{\text{COS}} + K_{\text{w}_2} P_{\text{H}_2\text{O}}} \quad (4.6)$$

Langmuir-Hinshelwood Model 2 (LH2)

$$-r_{\text{COS}} = \frac{k_2 K_{\text{C}_2} K_{\text{w}_2} P_{\text{COS}} P_{\text{H}_2\text{O}}}{(1 + K_{\text{C}_2} P_{\text{COS}})(1 + K_{\text{w}_2} P_{\text{H}_2\text{O}})} \quad (4.7)$$

In these models, the adsorption of the products, CO_2 and H_2S , as well as the reverse reaction rate, are neglected since the introduction of CO_2 or H_2S in the feed had no effect on the conversion of COS hydrolysis (Akimoto and Dalla Lana, 1979).

4.3.3 Model Discrimination Method

The proposed models for the hydrolysis of COS are nonlinear functions of the parameters. The search for model parameters by way of minimization of an objective function is an iterative process and therefore, requires an efficient optimization strategy.

Consider the nonlinear function,

$$-r_{\text{COS}} = f_{\text{model}}(\mathbf{C}, \mathbf{K}) + \epsilon \quad (4.8)$$

and its corresponding objective function,

$$\min. \{S(\mathbf{K})\} = \Sigma [(-r_i)_{\text{expl}} - f_{\text{model}}(\mathbf{C}, \mathbf{K})]^2 \quad (4.9)$$

where $\mathbf{C} = (C_{\text{COS}}, C_{\text{H}_2\text{O}})$ and $\mathbf{K} = (k_2, K_{\text{C}_2}, K_{\text{w}_2})^T$.

The Newton-Gauss technique was used to minimize the objective function, (4.9). It is based on linearization of the model equation by expansion as a Taylor series around an initial guess that $\mathbf{k} = \mathbf{K}$. It involves repetitive evaluation of

$$\Delta \mathbf{k}_i = (\mathbf{J}_i^T \cdot \mathbf{J}_i)^{-1} \mathbf{J}_i \epsilon_i \quad (4.10)$$

$$\mathbf{k}_{i+1} = \mathbf{k}_i + \Delta \mathbf{k}_i \quad (4.11)$$

until convergence is achieved. The symbols in (4.10) and (4.11) have the following meaning:

$$\mathbf{J}_i = \left\{ \mathbf{J}_{iLM} \right\} = \left\{ \frac{\partial f_{\text{model}}(\mathbf{C}_L, \mathbf{K})}{\partial \mathbf{K}_M} \right\}_{\mathbf{K}=\mathbf{k}_i} \quad (4.12)$$

$$\epsilon_i = (-r_i) - f_{\text{model}}(\mathbf{C}, \mathbf{K}_i) \quad (4.13)$$

A Fortran program (see Appendix D) was developed to find the model parameters. Table 4.1 and Table 4.2 present the regression parameters for each model (4.4), (4.5), (4.6) and (4.7) at the reaction temperature tested. If the parameters resulting from the regression of LH model functions are negative, they are considered to be unsuitable for representing the kinetic behavior of the hydrolysis of COS at the condition tested. If the convergence was forced to yield a positive result, the regression parameters showed a very large bias without statistical meaning. Some Data/LH model combinations show ill states. They either did not converge or converge to different values if different initial values were used. The value of parameter, n , obtained for the MER model function is close to 1.0. As a result of the above regression for the four model functions, the Eley-Rideal model appeared to provide the most suitable fit of the experimental data. But, as shown in Tables 4.1 and 4.2, the regression parameters for the ER model function still exhibit a large bias. The cause of this large bias could be attributed to the nonlinear property of the model/data set, as pointed out by Box (1971).

In Bates and Watts' "curvature measures", the nonlinearity of the model/data set combination is characterized by intrinsic nonlinearity (IN) and parameter nonlinearity (PE) (Bates and Watts, 1980). Table 4.3 presents the

Table 4.1. Regression Parameters of Model Functions (4.4), (4.5), (4.6) and (4.7)
for Alumina Kaiser 201

Model	Temp (°C)	k_2	Bias% (%)	K_{w2}	Bias% (%)		
(4.4)	270	0.848	0.0280	1235.66	46.42		
	300	1.179	0.0349	432.53	7.70		
	330	1.477	0.1640	215.95	9.28		
	Temp (°C)	k_2	Bias% (%)	K_{w2}	Bias% *%)	n	Bias% (%)
(4.5)	270	0.7312	92.36	4923.61	6509.28	0.978	0.216
	300	1.073	-2.942	650.11	149.94	0.979	0.24
	330	2.178	31.26	95.35	62.02	1.142	1.27
	Temp (°C)	k_2	Bias% (%)	K_{c2}	Bias% (%)	K_{w2}	Bias% (%)
(4.6)	270	-0.0365	3.097	-45.34	-0.12	17.54	6.20
	300	-0.0538	3.488	-46.28	0.21	15.79	5.02
	330	-0.24	3.197	-5.91	3.02	201.5	39.1
	Temp. (°C)	k_2	Bias% (%)	K_{c2}	Bias% (%)	K_{w2}	Bias% (%)
(4.7)	270	-0.361	16.70	-9.460	16.58	17.82	24.01
	300	2.709	86.83	-0.091	86.46	6557	5.364
	330	-7.053	74.64	333.1	99.30	-6413	41.54

Table 4.2. Regression Parameters of Model Functions (4.4), (4.5), (4.6) and (4.7) for Titania CRS 31

Model	Temp (°C)	k_2	Bias% (%)	K_{w2}	Bias% (%)		
(4.4)	270	0.832	0.022	625.63	11.21		
	300	1.307	0.059	274.10	5.43		
	330	2.088	0.425	148.02	11.11		
	Temp. (°C)	k_2	Bias% (%)	K_{w2}	Bias% (%)	n	Bias% (%)
(4.5)	270	0.830	-1.66	630.72	111.91	0.999	0.17
	300	1.324	25.55	264.40	76.81	1.004	6.99
	330	2.807	10.41	84.05	54.97	1.112	4.15
	Temp. (°C)	k_2	Bias% (%)	K_{c2}	Bias% (%)	K_{w2}	Bias% (%)
(4.6)	270	0.171	93.2	5.094	109.9	680.2	40.16
	300	-0.0005	-28.54	254.03	-0.0053	-285.9	1.273
	330	1.291	2142.1	1.634	2121.0	144.4	5.019
	Temp. (°C)	k_2	Bias% (%)	K_{c2}	Bias% (%)	K_{w2}	Bias% (%)
(4.7)	270	-0.889	390.9	-3.964	37.02	17.61	21.87
	300	-1.085	37.68	-4.878	35.60	16.67	22.24
	330	0.0513	7.15	-16490	10.92	-21560	22.23

calculated IN and PE values for the model function (4.4). The values of IN are well below the critical value while the PE values are above the critical value, indicating that the parameter-effect nonlinearity is responsible for the large bias of the estimated parameters.

Table 4.3. Curvature Measure of the Model Function (4.4) for Alumina Kaiser 201 and Titania CRS 31

Cat.	CRS 31		Kaiser 201	
Temp.	IN	PE	IN	PE
270°C	0.0222	1.4500	0.0266	2.8793
300°C	0.0371	1.0210	0.0293	1.1939
330°C	0.1084	1.4637	0.0615	1.2979

Critical value: $1/2(F)^{0.5} = 0.238$ at 95% confidence limit

4.3.4 Minimization of Bias of the Estimated Parameters

The bias of the estimated parameters can be reduced by using an appropriate reparameterization. But the "curvature measure" offers no guide to a suitable reparameterization. In a multi-parameter situation, it does not identify which parameter may be most responsible for the nonlinear behavior of the model function. In the following development, therefore, we combine the results from a simulation study, Box's bias calculation and the curvature measure to help suggest a useful reparameterization.

In a typical simulation study, 1000 sets of pseudo-random data, ϵ_{ij} , stochastically independent and identically normal in their distribution, were generated using the RNGET program on the mainframe MTS, which, in turn, gave rise to 1000 sets of estimates of (k_2, K_{w2}) from the objective function (4.14).

$$\min \{S(K_j)\} = \sum_{i=1}^N \left\{ [(-r_i)_{\text{exp}} + \epsilon_{ij}] - f_{\text{model}}(P_i, K_j) \right\}^2 \quad (4.14)$$

$$\epsilon_{ij}, j = 1, 2, \dots, 1000$$

For the concerned data/ER model (4.4), the results are presented as histograms in Figures 4.4 and 4.5. As Figures 4.4a and 4.5a show, the parameter k_2 possesses small bias and is close to a normal distribution. It seems reasonable to refer to the parameter k_2 as approximating linear behavior. On the other hand, the parameter K_{w2} , as shown in Figures 4.4b and 4.5b, exhibits a large bias and a strong positive skew from the normal distribution. These results suggest that K_{w2} is the parameter most responsible for the nonlinear behavior of the model/data set combination, characterized by the large PE numbers from the curvature measure. The following three reparameterized forms of the Eley-Rideal model function are proposed for the linearization of the nonlinear function.

Simple combination of k_2 and K_{w2} (SC):

$$-r_{\text{cos}} = \frac{\phi_2 P_{\text{cos}} P_{\text{H}_2\text{O}}}{1 + \phi_{w2} P_{\text{H}_2\text{O}}} \quad (4.15)$$

where $\phi_2 = k_2 K_{w2}$ and $\phi_{w2} = K_{w2}$.

Single reparameterization of K_w (SR):

$$-r_{\text{cos}} = \frac{\phi_2 P_{\text{cos}} P_{\text{H}_2\text{O}}}{\phi_{w2} + P_{\text{H}_2\text{O}}} \quad (4.16)$$

where $\phi_2 = k_2$ and $\phi_{w2} = 1/K_{w2}$.

Reparameterization of both k_2 and K_{w2} (BR):

$$-r_{\text{cos}} = \frac{P_{\text{cos}} P_{\text{H}_2\text{O}}}{\phi_2 + \phi_{w2} P_{\text{H}_2\text{O}}} \quad (4.17)$$

where $\phi_2 = 1/(k_2 K_{w2})$ and $\phi_{w2} = 1/k_2$.

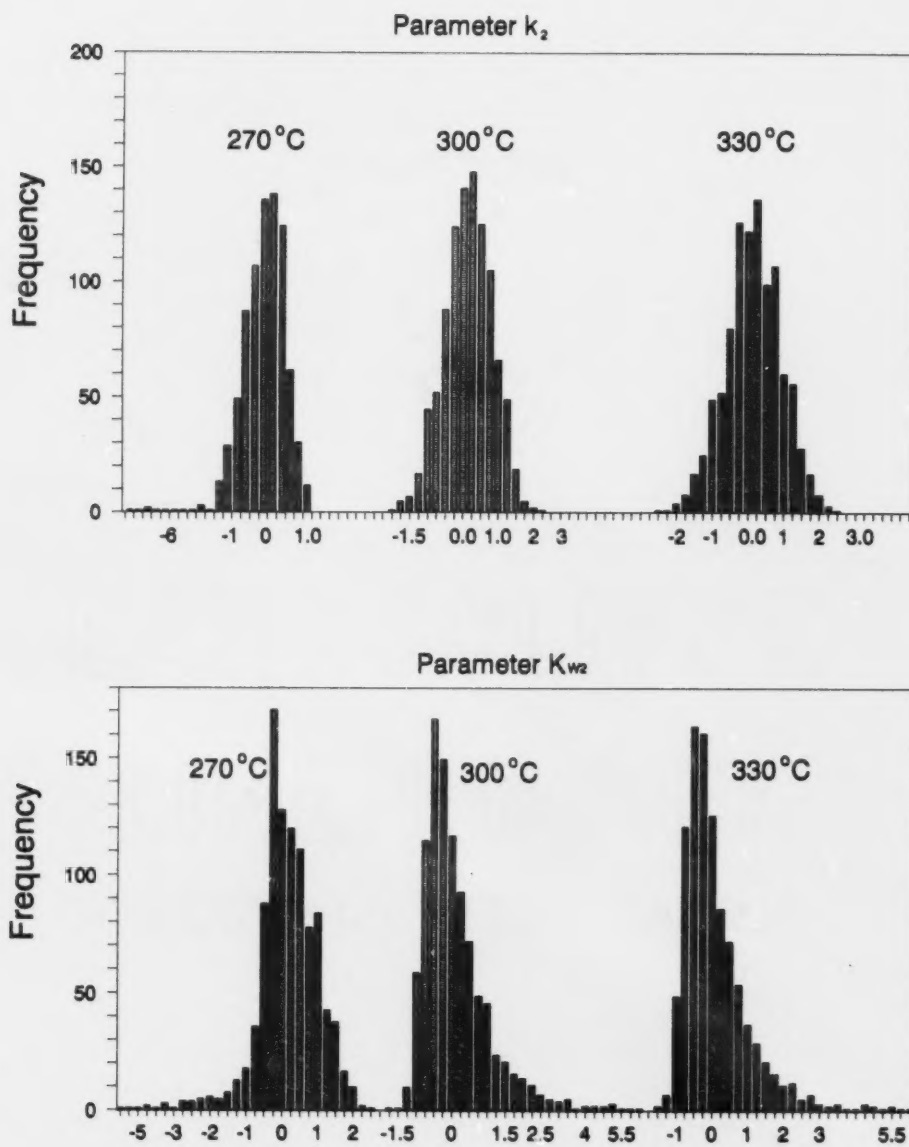
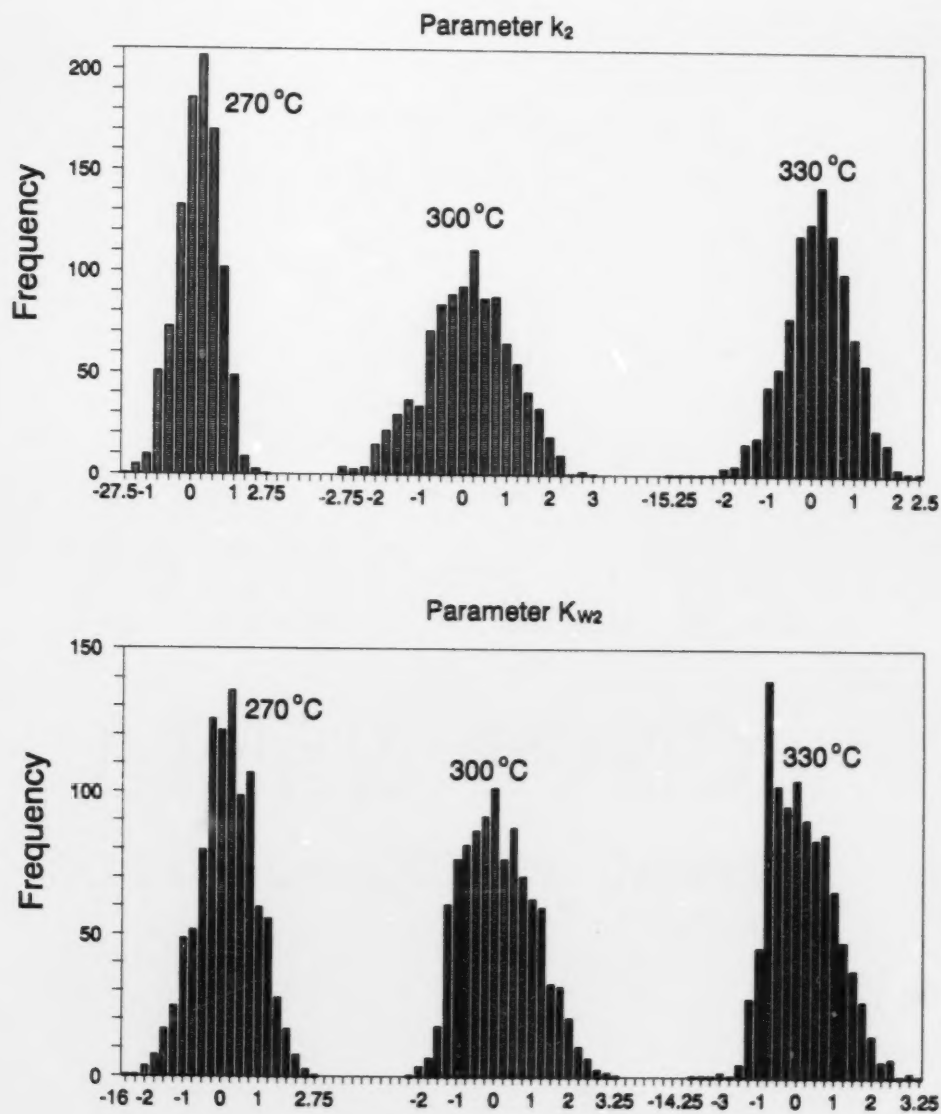
Figure 4.4 Histogram of Parameter k_2 and K_{w2} for Alumina Kaiser 201

Figure 4.5 Histogram of Parameter k_2 and K_{w2} for Titania CRS 31

Figures 4.6 and 4.7 present the resulting distribution of the parameter values obtained from the simulations using different forms of the Eley-Rideal model, (4.4), (4.15), (4.16) and (4.17) with the data set at 300°C. For each of the data sets at 270°C and 330°C, similar results were obtained. Table 4.4 summarizes the properties of the parameters from each reparameterized Eley-Rideal model function. As shown in Table 4.4, model function (4.17)/data set combination provides the parameter estimates with the closest to linear properties, that is, the smallest bias, smallest PE value and the closest to normal distribution.

4.3.5 Model Test

The estimates for the parameters of ϕ_2 and ϕ_{w2} , then k_2 and K_{w2} were subsequently obtained by regressing the Eley-Rideal model, (4.17). Table 4.5 presents the results for the parameter estimates, including the values of Student's t -test which is defined as

$$t = \frac{k}{S_k} \quad (4.18)$$

That is, the t value is the ratio of the parameter estimate, k , to its standard error, S_k . The high t values shown in Table 4.5, compared to t value of 1.73 at 0.05 significance level and 18 degree of freedom, indicate that the parameter estimates are well determined in the model. The numerical values of k_2 and K_{w2} presented in Table 4.5 were calculated from parameters, ϕ_2 and ϕ_{w2} , by the relations,

$$\phi_2 = 1/(k_2 K_{w2}), \quad \phi_{w2} = 1/k_2. \quad (4.19)$$

Comparing the k_2 and K_{w2} values calculated from equation (4.18) with those directly from the rate function (4.1), we find a small difference between the two sets of values, probably from the nonlinearity of model function (4.1) with a greater regression error and lower nonlinearity of model function (4.17) with a

Figure 4.6 Evolution of Parameter Distribution of ϕ_2 and ϕ_{w2}
for Alumina Kaiser 201 at 300°C Data Set

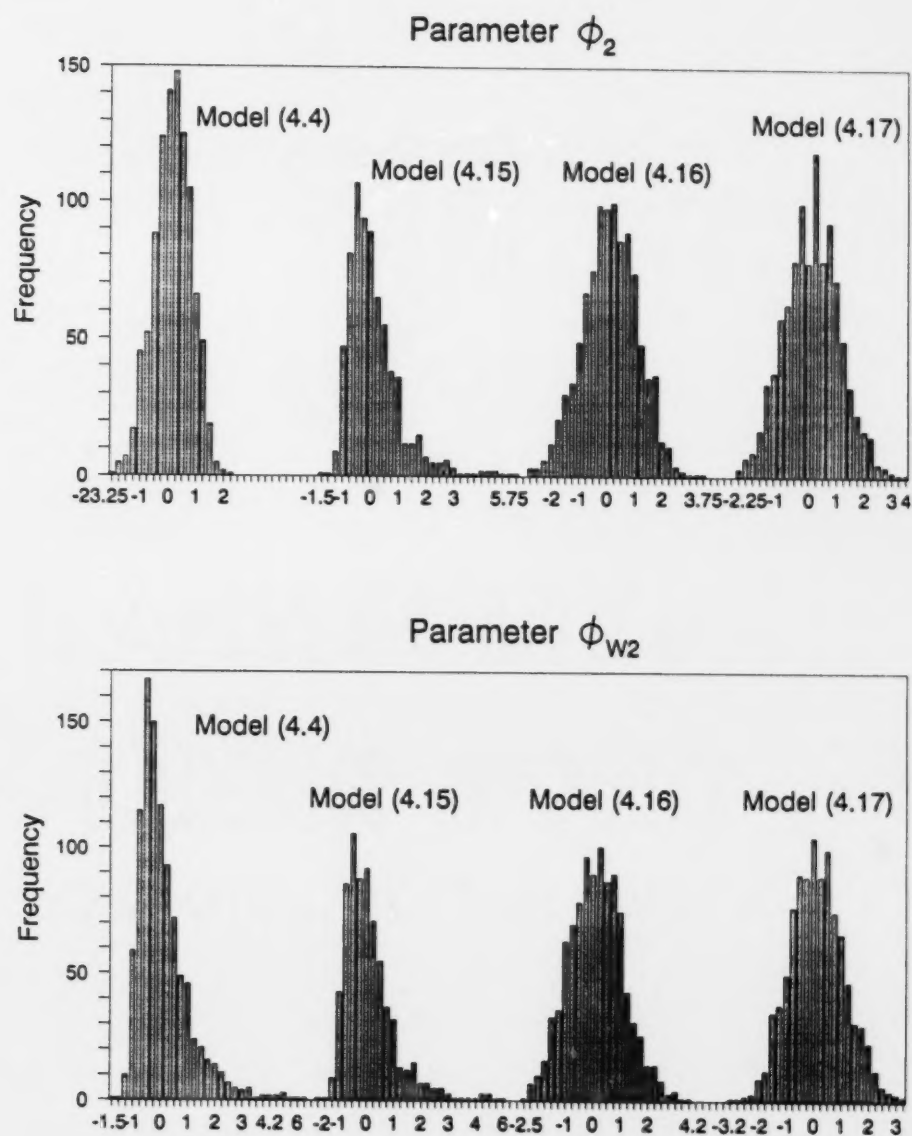


Figure 4.7 Evolution of Parameter Distribution of ϕ_2 and ϕ_{w2}
for Titania CRS 31 at 300°C Data Set

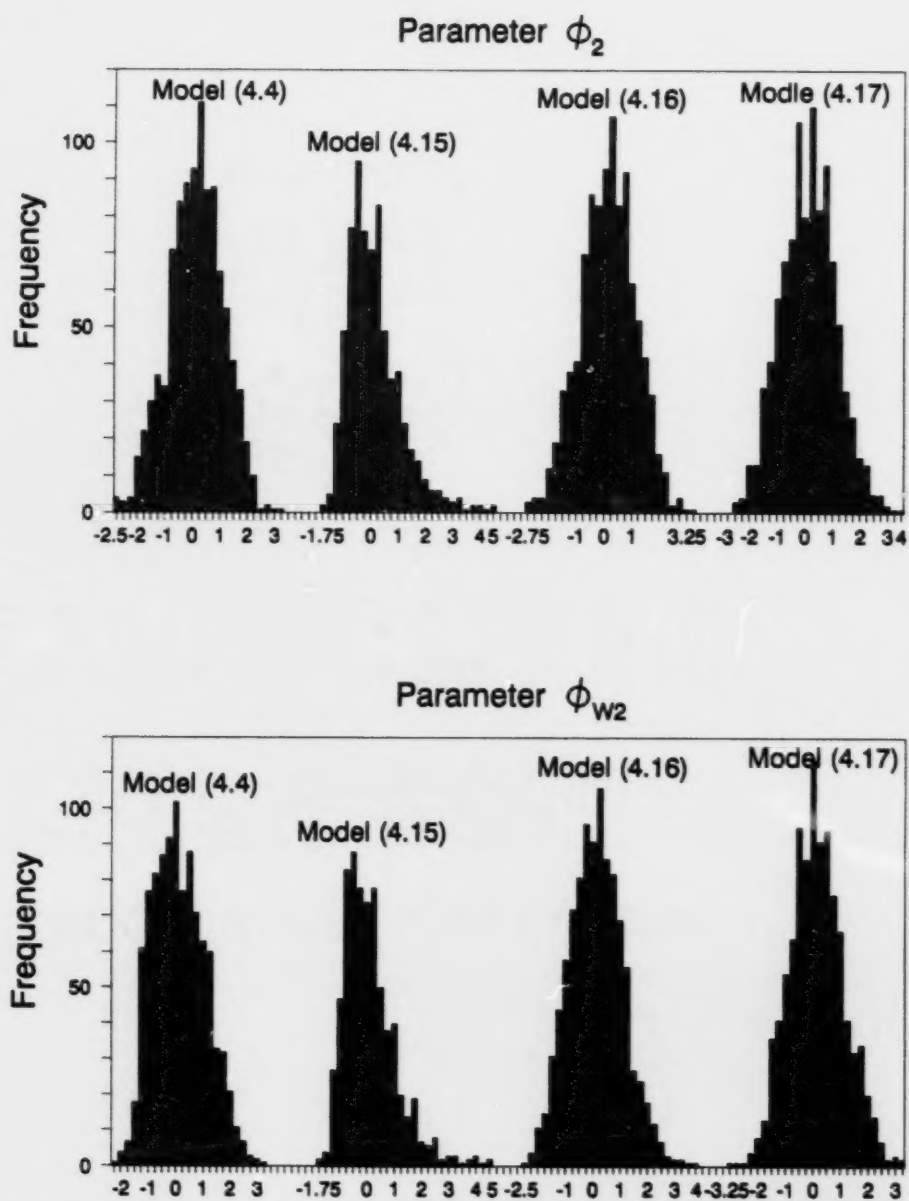


Table 4.4. Effect of Reparameterization for the Eley-Rideal Model
Function at 300°C Data Set

Kaiser 201	Bias (%)		Parameter Distribution *		PE
Equation	ϕ_2	ϕ_{w2}	ϕ_2	ϕ_{w2}	
(4.15)	7.23	7.69	1.92	1.92	0.74
(4.16)	0.035	0.97	-0.02	0.23	0.11
(4.17)	0.499	0.013	0.14	0.17	0.079

CRS 31	Bias%		Parameter Distribution *		PE
Equation	ϕ_2	ϕ_{w2}	ϕ_2	ϕ_{w2}	
(4.15)	4.940	5.43	1.35	1.36	0.61
(4.16)	0.059	1.07	-0.01	0.27	0.14
(4.17)	0.443	0.009	0.16	0.19	0.098

* Measures by skewness coefficient to normal distribution

Table 4.5 Regression Parameters From Model Function (4.17) for
Alumina Kaiser 201 and Titania CRS 31

Kaiser 201					
Temp. (°C)	ϕ_2	t	ϕ_{w2}	t	k_2 (mol/h·g·kPa)
270	8.80	3.61	18.0	50.1	0.00847
300	19.6	3.59	84.8	45.9	0.01179
330	31.4	3.25	67.7	20.9	0.01477

CRS 31					
Temp. (°C)	ϕ_2	t	ϕ_{w2}	t	k_2 (mol/h·g·kPa)
270	19.2	2.98	120.0	56.5	0.00832
300	27.9	4.27	76.5	35.6	0.01307
330	33.6	2.97	4.79	13.5	0.02088

lower regression error. In addition to the *t*-test on the adequacy of the parameters, an analysis of residuals was also carried out. The residual deviation, $[(-r_i)_{\text{expl}} - (-r_i)_{\text{model}}]$ is plotted against the predicted values of the response, $-r_{\text{model}}$, and is shown in Figures 4.8 and 4.9 for all the observations. The uniform bands for CRS 31 confirm the adequacy of the rate function at all temperatures and concentrations tested. But, for Kaiser 201, the residuals seem to be spread non-uniformly above and below $[(-r_i)_{\text{expl}} - (-r_i)_{\text{model}}] = 0$. This indicates that although the experimental data from Kaiser 201 is best-described by the Eley-Rideal model among the four models regressed, the most appropriate kinetic model has not yet been found for Kaiser 201 and remains to be searched more widely.

4.3.6 Comparison of Kinetic Parameters from Titania and from Alumina

As shown in the above model screening work, the hydrolysis of COS on both titania CRS 31 and alumina Kaiser 201 may be described by using the same type of Eley-Rideal model of the rate function though the catalytic activities of the two catalysts are different. In the ranges of temperature tested, the plots of k_2 versus $1/T$ and K_{w2} versus $1/T$, as shown in Figures 4.10 and 4.11, follow the Arrhenius law. Table 4.6 presents the kinetic parameters from the literature and from this experiment. The activation energy of alumina Kaiser 201 obtained from these plots compared well with those from other sources. The activation energy of titania CRS 31 measured herein appears to be the first "published" value. As shown in Table 4.6, the alumina catalyst Kaiser 201 had a smaller activation energy but a greater water adsorption equilibrium constant than those of titania, CRS 31. This difference further suggests that the strongly hydrophilic character of alumina inhibited the hydrolysis rate, which was reflected in the rate function by a

Figure 4.8 Residual Plotting for the Results From Alumina (Kaiser 201)

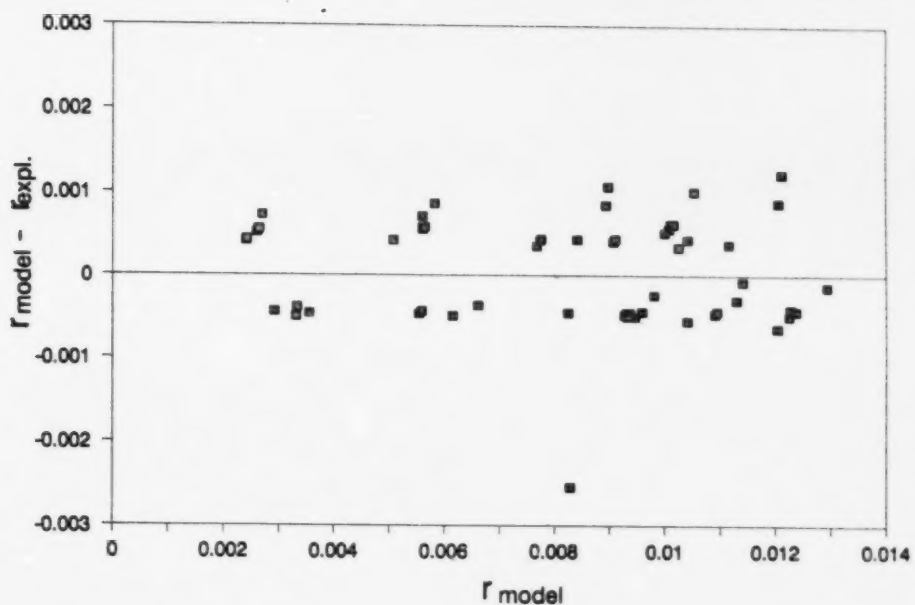
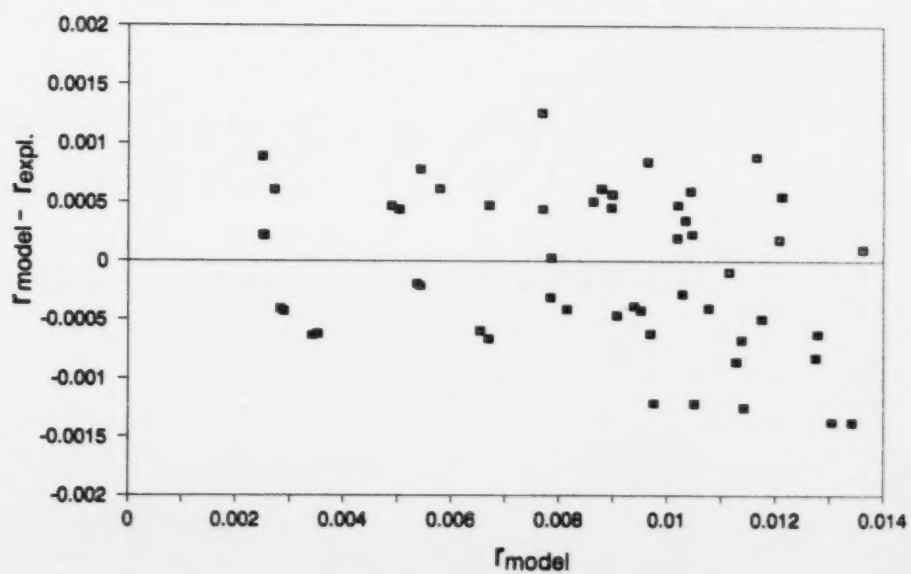


Figure 4.9 Residual Plotting for the Results From Titania (CRS 31)



large value of K_{w2} in the denominator. It has been verified that the base center on alumina catalyst was the functional catalytic active center responsible for the hydrolysis of COS (George, 1974). For the highly hydrophilic alumina catalyst, when covered by various types of adsorbed water, the crucial base centers for the hydrolysis of COS may not be well exposed. Figure 4.10 also shows that the two

Table 4.6 Comparison of Activation Energy From Different Sources

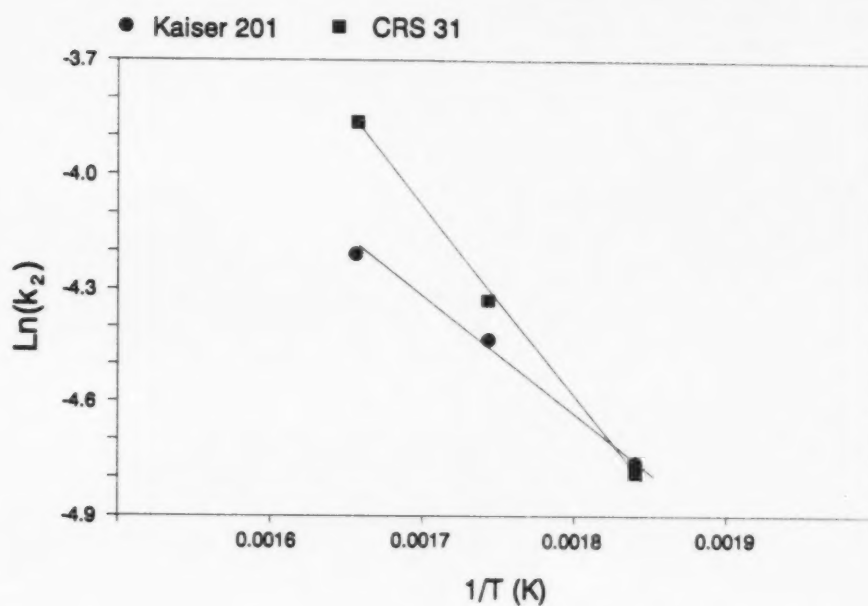
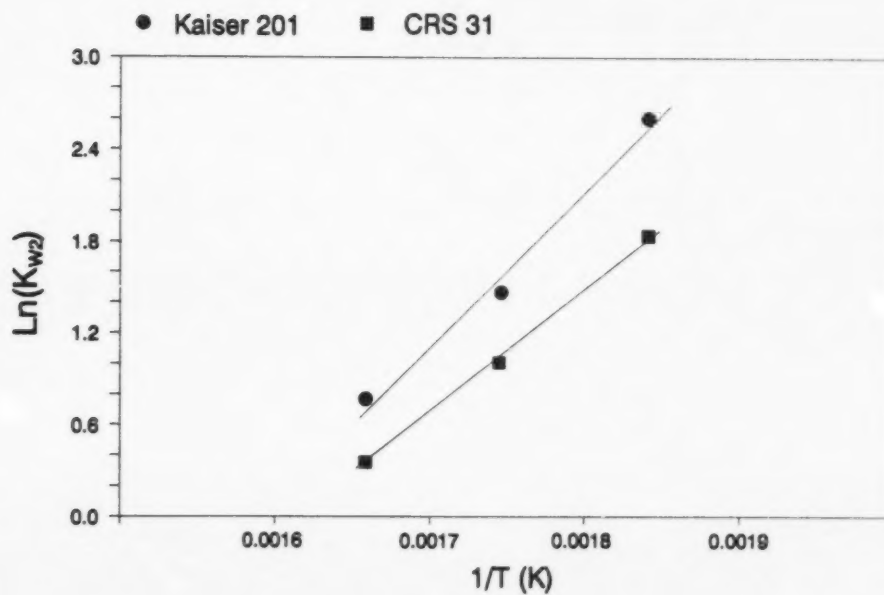
Catalyst	Temperature °C	Size mesh	E $\frac{\text{kcal}}{\text{mol}}$	H $\frac{\text{kcal}}{\text{mol}}$	Reference
Co-Mo/Al ₂ O ₃	320 – 378	20 – 40	12.0	–	a
NaOH/ γ -Al ₂ O ₃	196 – 290	20 – 40	4.2	–	b
γ -Al ₂ O ₃	196 – 290	20 – 40	4.8	–	b
γ -Al ₂ O ₃	80 – 120	40 – 60	6.3	243.1	c
Kaiser 201	270 – 330	25 – 30	6.04	19.89	d
CRS 31	270 – 330	25 – 30	9.98	16.10	d

a: George, 1974; b: Fiedorow, (1984); c: Zhang, 1988; d: This Work

$\ln(k_2)$ vs $1/T$ lines cross at temperature of 269°C. This inverse temperature phenomenon may be related to different water adsorption behavior of the two types of catalysts.

4.4 CONCLUSIONS

Intrinsic rate functions for the hydrolysis of COS catalyzed by either alumina (Kaiser 201) or titania (CRS 31) are both best-described by Eley-Rideal model over the range of temperature, 270° to 330°C. The regression parameters for the best-model function,

Figure 4.10 Arrhenius Plot of Parameter k_2 Figure 4.11 Arrhenius Plot of Parameter K_{w2} 

$$-r_{\text{COS}} = \frac{k_2 K_{w2} P_{\text{COS}} P_{\text{H}_2\text{O}}}{1 + K_{w2} P_{\text{H}_2\text{O}}} \quad (4.20)$$

are

Kaiser 201:

$$k_2 = \text{Exp}(0.835 - 3.039 \times 10^3/T), \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa}) \quad (4.21)$$

$$K_{w2} = \text{Exp}(-15.89 + 1.001 \times 10^4/T), \text{ 1/kPa} \quad (4.22)$$

$$E = 25.27, \text{ kJ/mol}$$

$$H = 83.22, \text{ kJ/mol}$$

and

CRS 31:

$$k_2 = \text{Exp}(4.45 - 5.024 \times 10^3/T), \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa}) \quad (4.23)$$

$$K_{w2} = \text{Exp}(-13.09 + 8.101 \times 10^3/T), \text{ 1/kPa} \quad (4.24)$$

$$E = 41.77, \text{ kJ/mol}$$

$$H = 67.35, \text{ kJ/mol}$$

The better hydrolysis activity of CRS 31 is suggested by its larger value for the pre-exponential factor and smaller value for K_{w2} over the temperature range tested. Adsorption of water inhibits COS hydrolysis on both catalysts but more so for Kaiser 201. Although a smaller activation energy for COS hydrolysis was observed on alumina Kaiser 201, the more stable adsorption of water on its surface, persistent even at more elevated temperature, likely blocks access of COS molecules to the active basic sites. These observations support the view that CRS 31 is the more effective catalyst over a wider range of temperatures. Since the partial pressure of water vapor in the converter of a modified Claus sulfur plant may exceed 20 % of the reaction pressure (about 1 atm), the rate-retarding influence of adsorbed water must be substantial.

4.5 NOMENCLATURE

E	=	Activation energy for the irreversible hydrolysis reaction, kJ/mol
f_{model}	=	Assumed model function
F	=	Statistical F test value
F_t	=	Total flow rate of the feed, m ³ /h
H	=	Heat of adsorption of water on the catalyst, kJ/mol
J_i	=	Jacobian matrix at the i th iteration
k	=	Parameter estimate
K	=	Parameter array, $(k_2, K_{c2}, K_{w2})^T$
k_2, K_{c2}, K_{w2}, n	=	Parameters of the rate functions
k_i	=	Parameter array at the i th iteration
K_M	=	The M th element of parameter array
N	=	Number of experimental observations
P	=	Partial pressure array, $(P_{\text{cos}}, P_{\text{H}_2\text{O}})$
P_{cos}	=	Partial pressure of COS, kPa
$P_{\text{H}_2\text{O}}$	=	Partial pressure of H ₂ O, kPa
P_L	=	The L th element of the partial pressure array
P_t	=	Total pressure of the reaction system, kPa
R	=	Gas constant, kJ/(mol·K)
$-r_{\text{cos}}$	=	Reaction rate of COS hydrolysis, mol/(h·g)
r_i	=	Rate at the i th observation
S_k	=	Standard error of parameter estimate
t	=	Student t test
T	=	Temperature, K

W	=	Catalyst mass, g
$(X_{\text{COS}})_{\text{in}}$	=	Inlet concentration of COS, mol %
$(X_{\text{COS}})_{\text{out}}$	=	Outlet concentration of COS, mol %

Greek Letters

ϵ	=	Difference between values of $(-r_i)$ obtained experimentally and from model prediction.
ϵ_{ij}	=	Random errors combined with experimental values of $(-r_i)$ during simulation.
ϕ_2, ϕ_{w2}	=	Parameters of reparameterized rate function.

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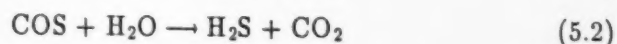
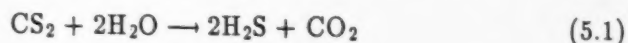
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CHAPTER 5

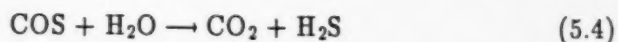
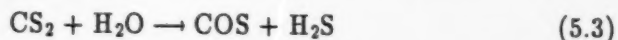
KINETICS STUDY OF CS_2 HYDROLYSIS WITH COS INTERMEDIATE

5.1 INTRODUCTION

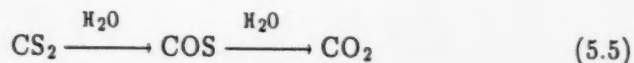
The hydrolysis of CS_2 and COS to the end products, H_2S and CO_2 , via the following stoichiometric equations was examined earlier (Chapters 3 and 4).



It was found that the activity of the titania (CRS 31), which is superior to that of the alumina catalyst above 290°C , appears to be related to the different water adsorption behavior on the surface of the two catalysts. It was also found that COS was formed during the CS_2 hydrolysis reaction and that the titania-catalyzed CS_2 hydrolysis produced less COS in the effluent than the alumina. This observation was explained in Chapter 3 by the consecutive reactions:



or in a simplified form:



All catalysts tested catalyzed the second step faster than the first step of the consecutive reaction (5.5).

To further clarify the water effect and kinetic behavior for CS_2 and COS hydrolysis on the two catalysts, Kaiser 201 and CRS 31, rate functions were obtained for COS hydrolysis over both titania (CRS 31) and alumina (Kaiser 201) in Chapter 4. In this Chapter, rate functions for CS_2 hydrolysis are to be established for both alumina (Kaiser 201) and titania (CRS31).

It has long been thought that CS_2 is hydrolyzed to end products, CO_2 and H_2S , via COS intermediate as per the consecutive reaction (5.5) (Akimoto and Dalla Lana, 1979), but a detailed kinetics treatment for the simultaneous CS_2 and

COS hydrolysis describing the range of temperatures encountered in the first Claus converter has not yet been reported in the literature. Moreover, Nethem and Gati (1990) have reported an alternative path for the formation of COS,



which may lead to an additional complication for the kinetics of CS_2 hydrolysis. If the reaction (5.6) can proceed simultaneously with the hydrolysis of CS_2 and COS, an auto-catalytic behavior should be observed for the hydrolysis of CS_2 since the CO_2 produced in reaction (5.4) should accelerate the conversion of CS_2 through reaction (5.6). Therefore, in the establishment of the CS_2 hydrolysis rate function, whether or not CO_2 will interfere with the CS_2 hydrolysis rate should be first clarified. The purpose of this part of the work is to complete the kinetics description of CS_2 and COS hydrolysis on the two catalysts: Kaiser 201 and CRS 31.

5.2 EXPERIMENTAL

5.2.1 Method

Both CS_2 and COS hydrolysis rates were again measured using a Berty type reactor. At each reaction temperature tested, the total gas flow rate ($\text{CS}_2 + \text{H}_2\text{O} + \text{N}_2$) was maintained at $0.03 \text{ m}^3/\text{h}$. and 150 kPa . High purity N_2 (99.99 %) was obtained from Matheson (Edmonton) and CS_2 (analytical reagent, > 99.9 %) was obtained from BDH Chemicals. To study the pressure dependence, the partial pressure of CS_2 and H_2O were regulated as follows: two streams of known flow rates of N_2 were maintained by mass flow controllers. Then, the two N_2 gas streams were passed through either a thermostatted bubbler holding ion-free water or one holding CS_2 liquid. Thus, at each predetermined value of the vapor

pressure of either CS_2 or H_2O , regulated by the bath temperatures, a partial pressure ranging from 0.75 to 3 kPa (0.5 to 2.0 mol %) for CS_2 and from 3 to 18 kPa (2 to 12 mol %) for water vapor could be preset. The detailed calculation of the CS_2 and COS concentrations from the GC analysis and the determination of CS_2 and COS hydrolysis rates can be found in Appendix B.

In the test of possible H_2S or CO_2 effects on CS_2 hydrolysis, the experimental procedure was arranged according to the the following method: first, a set of conversions of CS_2 hydrolysis under steady-state conditions ranging from 230°C to 340°C was obtained. Then, a predetermined flow of CO_2 , maintained by a mass flow controller, was introduced into the reactor in place of some of the nitrogen in the feed stream, and the conversion of CS_2 hydrolysis at steady-state was measured again in the same range of operating temperatures. This procedure was repeated for the testing of the effect of H_2S upon CS_2 hydrolysis.

Prior to the measurements of the rate of reaction, the catalysts were crushed to test the effect of particle size on internal diffusion for the hydrolysis of CS_2 . Figure 5.1 shows that the internal diffusion effect is eliminated when the catalyst particle size is not larger than +20–25 mesh size. In each experiment, 2 g of catalyst were used. The reaction mixture was preheated before entering the reactor. A detailed description of the equipment, operating procedure, and the feed-product analysis can be found in Chapter 2.

5.2.2 Catalyst

As a continuation of the previous work on the kinetics of COS hydrolysis on alumina (Kaiser 201) and titania (CRS 31), the same catalysts were used for the kinetics study of CS_2 hydrolysis. The physical properties of the catalysts can be found in the experimental section of Chapter 4.

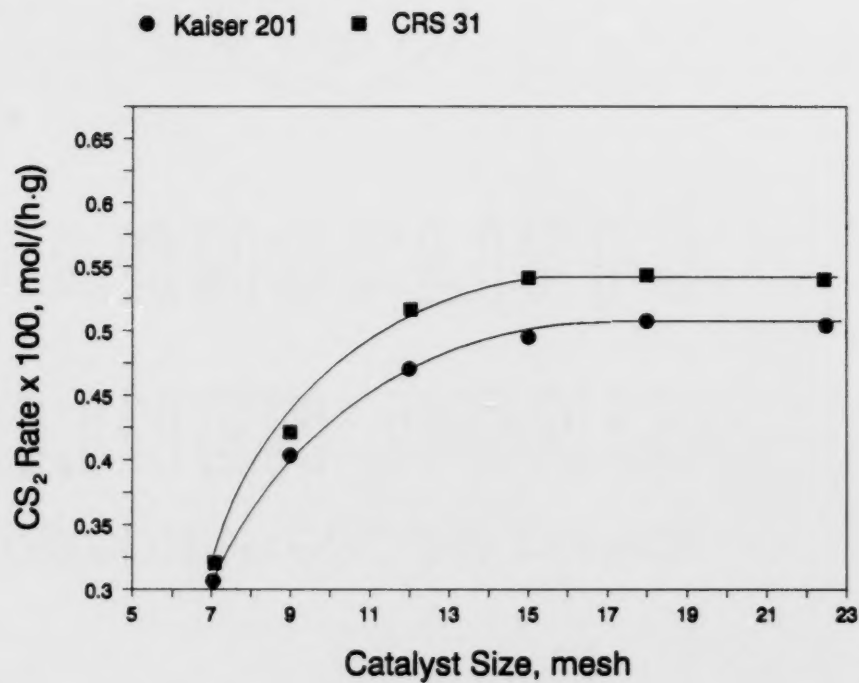
Figure 5.1 Effect of Catalyst Particle Size on CS₂ Hydrolysis

Test Conditions:

Temperature = 330°C, Pressure 150 kPa, Feed Flowrate = 0.03 m³/h

Feed Composition, mol %: CS₂ = 1.09, H₂O = 2.05, N₂ = 96.86

Catalyst Weight = 2.0 g



5.3 RESULTS AND DISCUSSION

5.3.1 The Influence of CO₂ and H₂S Upon CS₂ Hydrolysis

In the Berty reactor, the CS₂ hydrolysis reaction with a feed composition of 2 mol % CS₂ and 5.4 mol % H₂O was carried out between 230 and 340°C. After the catalyst activity reached a steady-state, which procedure was described in the experimental section for the kinetics study of COS hydrolysis, the conversion of CS₂ was measured. Then, 2.0 mol % of either CO₂ or H₂S were added to the feed stream, and the measurement of CS₂ conversion was repeated within the same range of reaction temperatures. The conversion of CS₂ is calculated by equation (5.7):

$$\text{CS}_2 \text{ Conv. \%} = \frac{(X_{\text{CS}_2})_{\text{in}} - (X_{\text{CS}_2})_{\text{out}}}{(X_{\text{CS}_2})_{\text{in}}} \times 100 \% \quad (5.7)$$

Figure 5.2 presents the results of CS₂ conversion obtained with or without the presence of CO₂ (or H₂S) for both the alumina and titania. It shows that the introduction of CO₂ or H₂S does not affect the conversion for the hydrolysis of CS₂. This indicates that the reaction (5.6) does not proceed along with the hydrolysis reactions (5.3) and (5.4), and it also implies that the reverse rate of the hydrolysis reaction is negligible under the test conditions. In Nemeth and Gati's work (1990), the kinetics experiments suggested that the reaction of strongly adsorbed CO₂ on the alumina catalyst with physisorbed or gas-phase CS₂ is a possible mechanism for reaction (5.6), and the surface basic sites on the alumina catalyst are the catalytic centers for reaction (5.6). These observations agree with the kinetics phenomena observed in the hydrolysis reactions which are also

Figure 5.2 Effect of H_2S or CO_2 on CS_2 Hydrolysis

Temperature = 230 to 340°C, Pressure = 150 kPa,

Feed Flowrate = 0.03 m³/h

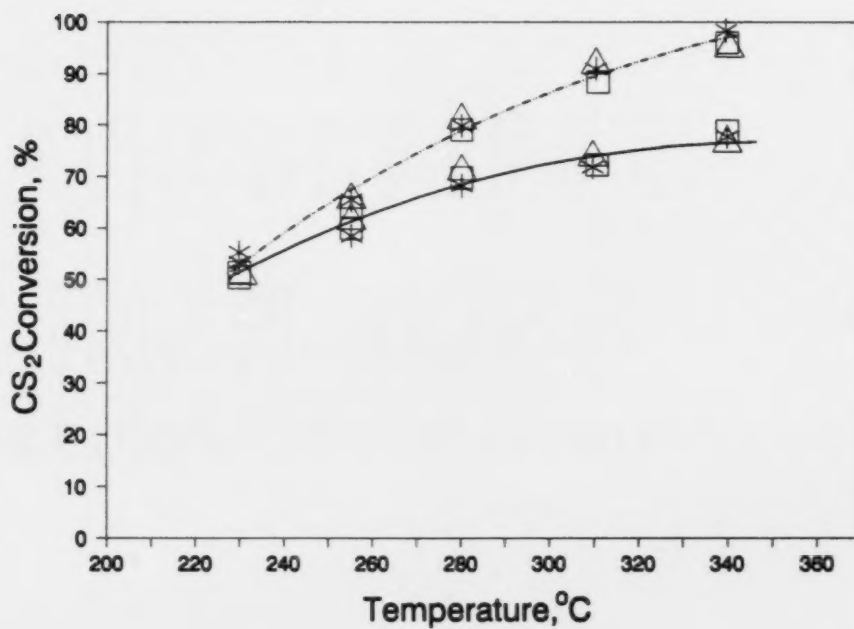
Feed Composition, vol %:

Δ — $\text{CS}_2 = 2.0$, $\text{H}_2\text{O} = 5.4$, $\text{N}_2 = 92.6$

* — $\text{CS}_2 = 2.0$, $\text{H}_2\text{O} = 5.4$, $\text{H}_2\text{S} = 2.2$, $\text{N}_2 = 90.4$

$\square$ — $\text{CS}_2 = 2.0$, $\text{H}_2\text{O} = 5.4$, $\text{CO}_2 = 2.1$, $\text{N}_2 = 90.5$

--- Titania (CRS 31), — Alumina (Kaiser 201)



catalyzed by surface basic sites (Fiedorow, et al., 1984; George, 1974) and which correlate with an Eley-Rideal mechanism (Chapters 4 and 5). One of the explanations for the behavior shown in Figure 5.2 is that when water is present in the system, its strong adsorption on the catalyst surface interferes with the weaker adsorption of compounds such as CO_2 and H_2S on the surface. Therefore, the CO_2 produced from reaction (5.4) does not react with CS_2 to produce COS via reaction (5.6) because it may be inhibited by the strongly adsorbed H_2O on the catalyst surface. Since the formation of COS via reaction (5.6) does not occur in the system of the hydrolysis reactions of CS_2 , the formation of COS from CS_2 hydrolysis via the consecutive reaction (5.5) appears to be the likely route.

5.3.2. Establishment of CS_2 Hydrolysis Rate Functions

Vapor-phase hydrolysis of CS_2 over a broad range of feed compositions (CS_2 : 0.5 to 2 mol %; H_2O : 2 to 12 mol %) was performed using the laboratory Berty reactor. The reaction rate of CS_2 hydrolysis in the Berty type reactor is calculated using equation (5.8).

$$-r_{\text{CS}_2} = \frac{(X_{\text{CS}_2})_{\text{in}} - (X_{\text{CS}_2})_{\text{out}}}{W} \times \frac{F_t \cdot P_t}{R \cdot T}, \quad \text{mol/g} \cdot \text{h} \quad (5.8)$$

Figures 5.3 and 5.4 show the changes in the CS_2 hydrolysis rate as a function of H_2O partial pressure at various inlet CS_2 levels on the alumina and the titania. As shown in the figures, the intrinsic hydrolysis rate of CS_2 approaches a constant value with the increase of partial pressure of water for both the alumina and the titania at each reaction temperature (270, 300 and 330°C) tested. On the other hand, an increase in inlet CS_2 partial pressure proportionally increases the

Figure 5.3 Intrinsic Rate of CS₂ Hydrolysis Catalyzed by Alumina (Kaiser 201)

Test Conditions:

Temperature = 270 to 330°C, Pressure = 150 kPa, Feed Flowrate = 0.03 m³/h

Catalyst Weight = 2.00 g

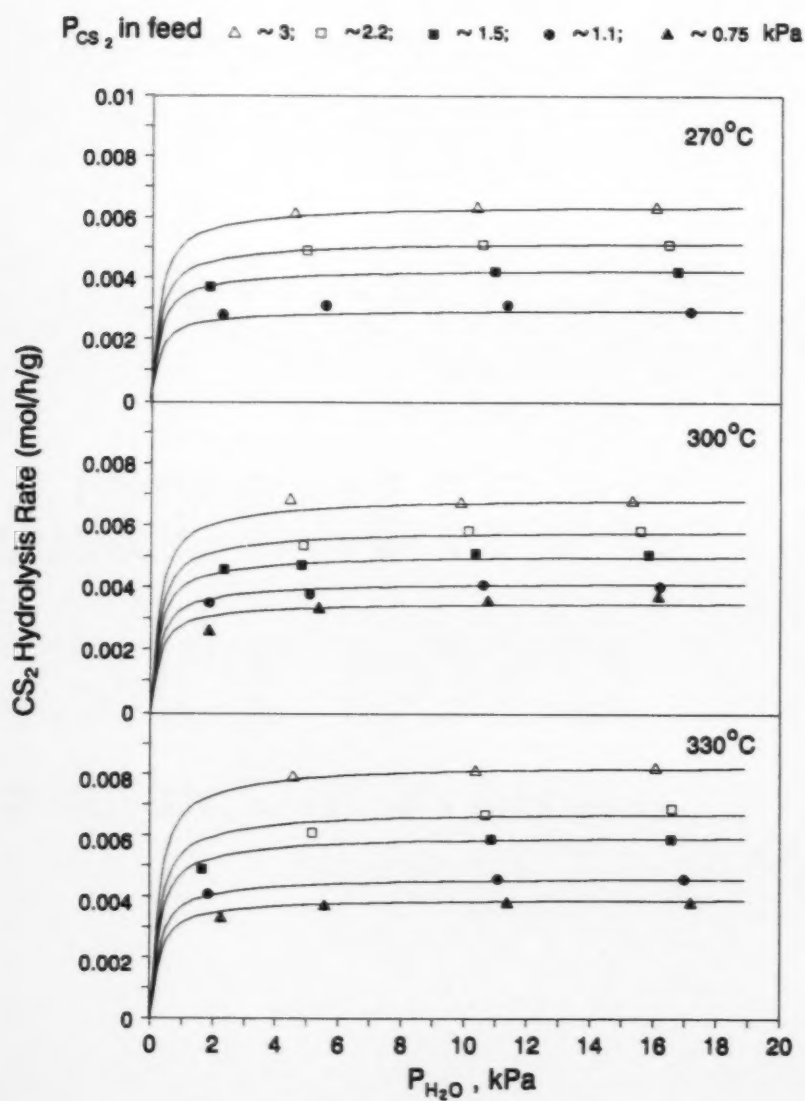


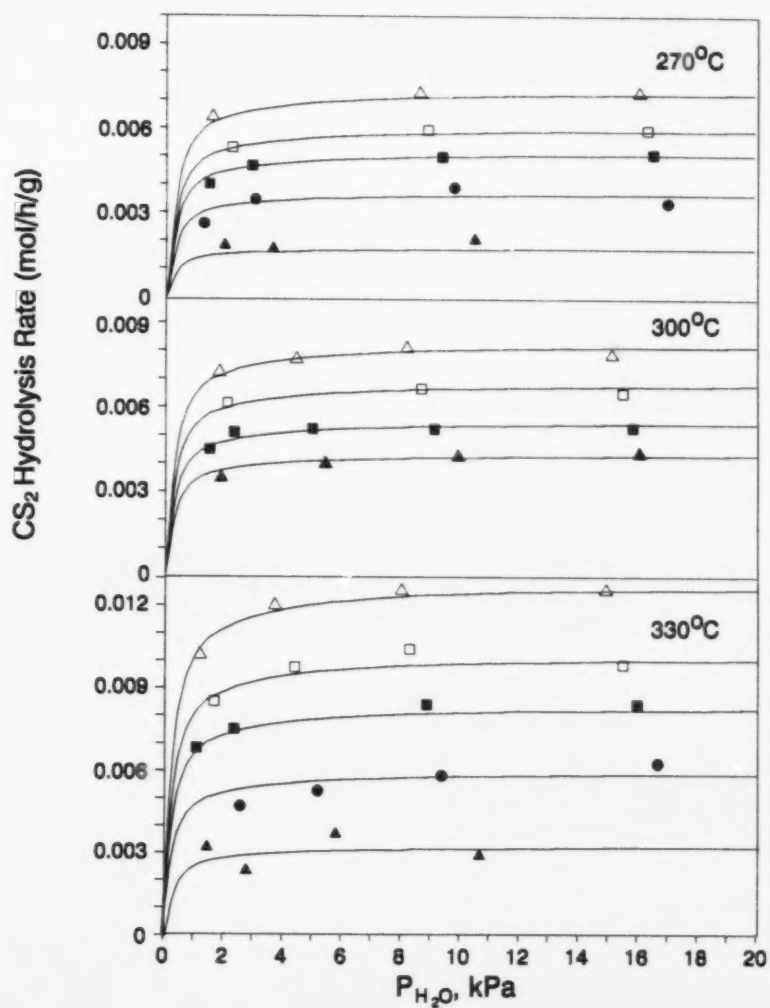
Figure 5.4 Intrinsic Rate of CS₂ Hydrolysis Catalyzed by Titania (CRS 31)

Test Conditions:

Temperature = 270 to 330°C, Pressure = 150 kPa, Feed Flowrate = 0.03 m³/h

Catalyst Weight = 2.00 g

P_{CS₂} in feed: $\triangle$ ~3; $\square$ ~2.2; $\blacksquare$ ~1.5; $\bullet$ ~1.1; $\blacktriangle$ ~0.75 kPa



intrinsic CS₂ hydrolysis rate, more apparent for the titania than for the alumina. By considering the above experimental facts and the observation that the introduction of CO₂ or H₂S shows no effect on the CS₂ hydrolysis rate and that COS is found in the effluent from the Berty reactor during the CS₂ hydrolysis reaction, the following mathematical rate expressions based on the Eley-Rideal mechanism and the Langmuir-Hinshelwood approach are chosen to fit the experimental data:

Eley-Rideal Model 1 (ER1)

$$-r_{\text{CS}_2} = \frac{k_1 K_w P_{\text{CS}_2} P_{\text{H}_2\text{O}}}{(1 + K_w P_{\text{H}_2\text{O}})} \quad (5.9)$$

Eley-Rideal Model 2 (ER2)

$$-r_{\text{CS}_2} = \frac{k_1 K_w P_{\text{CS}_2} P_{\text{H}_2\text{O}}}{(1 + K_c P_{\text{COS}} + K_w P_{\text{H}_2\text{O}})} \quad (5.10)$$

Langmuir-Hinshelwood Model 1 (LH1)

$$-r_{\text{CS}_2} = \frac{k_1 K_w P_{\text{CS}_2} P_{\text{H}_2\text{O}}}{(1 + K_c P_{\text{COS}} + K_d P_{\text{CS}_2} + K_w P_{\text{H}_2\text{O}})^2} \quad (5.11)$$

Langmuir-Hinshelwood Model 2 (LH2)

$$-r_{\text{CS}_2} = \frac{k_1 K_w P_{\text{CS}_2} P_{\text{H}_2\text{O}}}{(1 + K_c P_{\text{COS}} + K_d P_{\text{CS}_2})(1 + K_w P_{\text{H}_2\text{O}})} \quad (5.12)$$

The assumptions used for obtaining the above rate expressions are summarized in Table 5.1, in addition to the assumptions underlying the Langmuir isotherm: homogeneous surface, no interaction between adsorbed species on the catalyst surface. Detailed mathematical derivations can be found in Appendix C. Tables

Table 5.1 Assumptions Implicit in the Form of Rate Functions for CS₂ Hydrolysis

Model	Assumptions
ER 1	a. Rate controlling step: Gas phase or physisorbed CS₂ reacts with H₂O adsorbed on the surface. b. The fraction of surface occupied by adsorbed CS₂, COS, CO₂ and H₂S is negligible.
ER 2	a. Rate Controlling Step: Gas phase or physisorbed CS₂ reacts with H₂O adsorbed on the surface. b. The fraction of surface occupied by adsorbed CS₂, CO₂ and H₂S is negligible. c. COS and H₂O adsorbed on the same sites.
LH 1	a. Rate Controlling Step: Adsorbed CS₂ on the surface reacts with adsorbed H₂O on the surface. b. The fraction of surface occupied by adsorbed CO₂ and H₂S is negligible. c. All the species are adsorbed on the same site on the surface.
LH 2	a. Rate Controlling Step: Adsorbed CS₂ on the surface reacts with adsorbed H₂O on the surface. b. The fraction of surface occupied by CO₂ and H₂S is negligible. c. Two types of active sites are present on the surface. CS₂ and COS are adsorbed on one type of active site. H₂O is adsorbed on another type of active site.

5.2 and 5.3 present the regressed results for Kaiser 201 and CRS 31 respectively. By examination of the standard error of the regression parameters for each model at each temperature tested and also the Arrhenius plots shown in Figures 5.4 and 5.5, the regression parameters from the Eley-Rideal model are seen to follow the Arrhenius law (or the Van't Hoff equation) with smaller standard errors than those from other models. The parameters of the rate functions from other models show either large standard errors or disobey the Arrhenius law (or the Van't Hoff equation) in the range of temperatures tested. For Kaiser 201, model LH2 exhibits negative parameters; model LH1 shows very large standard errors for the regression parameters; and model ER2 shows large standard errors for the parameters and a nonlinear relationship between $\ln(K_{d1})$ and $1/T$. For CRS 31, the rate functions from models ER2, LH1 and LH2 all converge to negative parameters for the sets of experimental data obtained. From the above results, only model ER1 gives rational parameters for both alumina (Kaiser 201) and titania (CRS 31). Of the four intrinsic rate functions tested for the hydrolysis of CS_2 , catalyzed by either alumina (Kaiser 201) or titania (CRS 31), the Eley-Rideal model appears to best-fit over the range of temperatures, 270 to 330°C, tested. The regression parameters for the best-fitting model:

$$-r_{\text{CS}_2} = \frac{k_1 K_{w1} P_{\text{CS}_2} P_{\text{H}_2\text{O}}}{(1 + K_{w1} P_{\text{H}_2\text{O}})} \quad (5.13)$$

are

Kaiser 201:

$$k_1 = \text{Exp}(3.037 - 4.891 \times 10^3/T) \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa}) \quad (5.14)$$

$$K_{w1} = \text{Exp}(-19.49 + 1.184 \times 10^4/T) \text{ 1/kPa} \quad (5.15)$$

$$E = 40.66 \text{ kJ/mol}, \quad A = 20.84 \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa})$$

Table 5.2 Regressed Parameters from Various Models (Kaiser 201)

Model	T (°C)	k ₁	StdErr	K _{w1}	StdErr		
ER 1	270	2.77E-3	4.10E-5	11.0	1.19E0		
	300	3.44E-3	1.43E-4	2.63	1.49E0		
	330	6.85E-3	4.52E-5	1.27	6.84E-2		
	T (°C)	k ₁	StdErr	K _{c1}	StdErr	K _{w1}	StdErr
ER 2	270	2.80E-3	3.34E-5	4.56E+4	1.01E+4	4.14E+4	1.04E+4
	300	3.57E-3	1.64E-4	5.02E+4	3.89E+7	1.20E+4	9.23E+6
	330	6.87E-3	4.74E-5	1.25E0	1.02E0	1.49E0	1.98E-1
	T (°C)	k ₁	StdErr	K _{c1}	StdErr	K _{d1}	StdErr
LH 1	270	2.79E+2	1.59E+7	2.79E-2	1.59E+3	5.76E+3	9.04E+5
	300	3.17E+2	9.41E+6	3.17E-2	9.42E+2	5.26E+3	6.61E+5
	333	4.13E+2	1.47E+7	4.13E-2	1.47E+3	4.38E+3	5.60E+5
	T (°C)	K _{w1}	StdErr				
	270	1.18E+2	1.87E+4				
	300	1.08E+2	1.36E+4				
	330	9.77E+1	1.27E+4				
	T (°C)	k ₁	StdErr	K _{c1}	StdErr	K _{d1}	StdErr
LH 2	270	5.64E-2	2.45E-1	5.16E-2	2.22E-1	-3.25E-1	2.86E0
	300	6.41E-2	2.30E-1	7.65E-2	2.70E-1	1.53E0	2.88E0
	333	6.63E-3	2.13E-3	8.08E-1	2.57E-1	-7.62E0	2.20E0
	T (°C)	K _{w1}	StdErr				
	270	9.05E0	7.19E0				
	300	1.63E0	4.97E-1				
	330	-2.20E4	3.12E+4				

Table 5.3 Regressed Parameters from Various Models (CRS 31)

Model	T (°C)	k ₁	StdErr	K _{w1}	StdErr		
ER 1	270	3.31E-3	2.96E-5	5.63	1.11E0		
	300	5.46E-3	3.82E-5	2.47	1.78E-1		
	330	1.16E-2	8.94E-4	0.35	7.49E-2		
	T (°C)	k ₁	StdErr	K _{c1}	StdErr	K _{w1}	StdErr
ER 2	270	5.46E-3	4.03E-5	1.94E-1	2.86E0	2.50E0	5.00E-1
	300	3.31E-3	3.25E-5	-1.11E0	5.47E0	5.18E0	2.65E0
	330	1.04E-2	8.62E-4	-1.03E0	2.93E0	2.27E-1	5.01E-2
	T (°C)	k ₁	StdErr	K _{c1}	StdErr	K _{d1}	StdErr
LH 1	270	7.17E-2	9.94E-2	2.36E-1	3.55E-1	-2.39E0	5.87E0
	300	2.85E-2	1.81E-2	8.96E-1	5.54E-1	-1.35E1	9.12E0
	333	1.09E-1	3.14E-2	3.71E-1	1.25E-1	-5.94E0	2.12E0
	T (°C)	K _{w1}	StdErr				
	270	1.80E-1	1.85E-2				
	300	1.79E-1	1.73E-2				
	330	1.36E-1	1.87E-2				
	T (°C)	k ₁	StdErr	K _{c1}	StdErr	K _{d1}	StdErr
LH 2	270	5.78E-2	1.72E+4	5.37E-2	1.60E+4	-2.63E0	1.86E+5
	300	1.27E-1	1.34E+4	3.73E-2	3.94E+3	-1.18E1	1.26E+6
	333	2.24E-1	3.73E0	3.06E-2	5.08E-1	3.98E1	6.23E+2
	T (°C)	K _{w1}	StdErr				
	270	4.84E+3	9.44E+3				
	300	6.00E+3	2.24E+4				
	330	-2.17E4	1.73E+5				

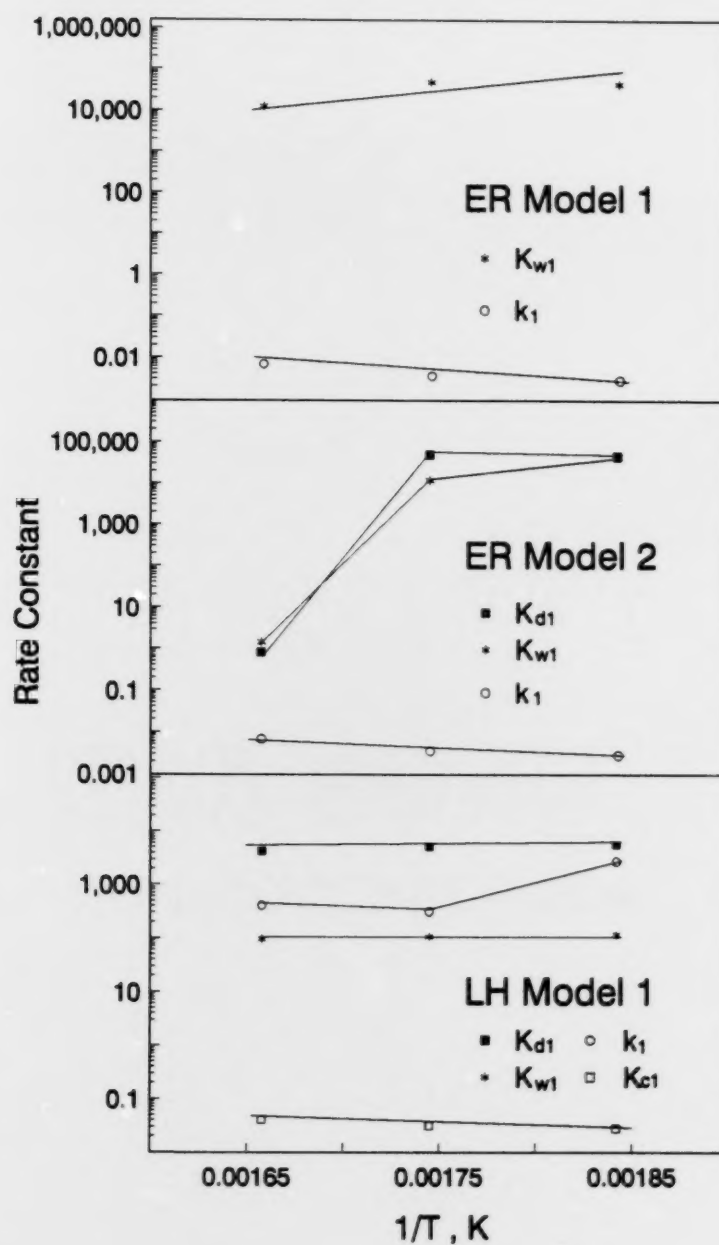
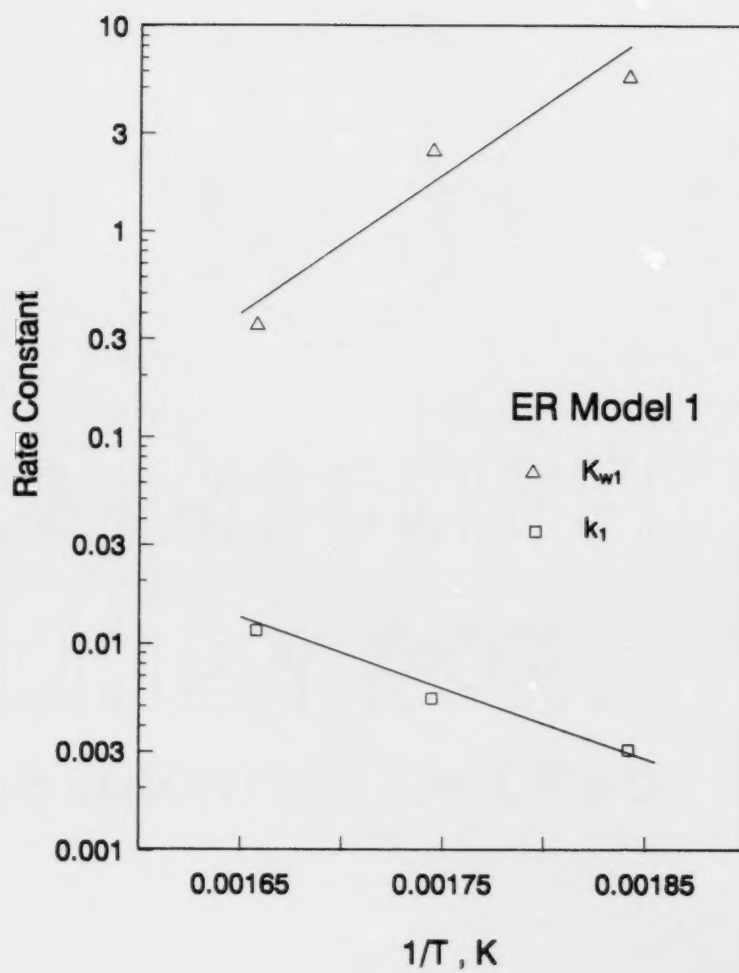
Figure 5.5 Plots of the Rate Function Parameters Versus $1/T$ (Kaiser 201)

Figure 5.6 Plots of the Rate Function Parameters Versus $1/T$ (CRS 31)

Titania CRS 31:

$$k_1 = \text{Exp}(6.786 - 6.813 \times 10^3/T) \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa}) \quad (5.16)$$

$$K_{w1} = \text{Exp}(-25.76 + 1.104 \times 10^4/T) \text{ 1/kPa} \quad (5.17)$$

$$E_a = 56.64 \text{ kJ/mol}, \quad A = 8.854 \times 10^2 \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa})$$

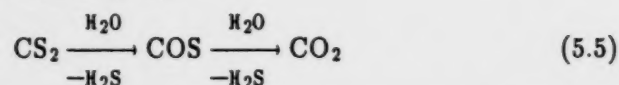
It can be seen from the comparison of the rate constant, k_1 , between alumina (Kaiser 201) and titania (CRS 31) that the greater activation energy for titania is compensated for by its correspondingly greater pre-exponential factor. This fact, together with its smaller value for K_{w1} relative to that of alumina, suggests why titania exhibits the higher catalytic activity for the hydrolysis of CS_2 . With increasing reaction temperature, the difference in the k_1 constants between titania and alumina becomes increasingly larger, which kinetically explains the earlier result that CS_2 hydrolysis activity on titania exceeds that on alumina above 290°C . The larger K_{w1} value for the inherently hydrophilic alumina may be responsible for its smaller pre-exponential factor which can be attributed to fewer surface basic sites being available on a highly "wetted" surface. The overwhelmingly high concentration of adsorbed water molecules on the surface reduces the availability of exposed surface basic sites.

Although the experimental kinetics data are best-described by the Eley-Rideal model among the models tested, it does not represent the reaction mechanism truly occurring on the surface. By the comparison of the lines in Figure 5.3 with those in Figure 5.4, titania CRS 31 exhibits a more scatter distribution than the alumina Kaiser 201. At the highest temperature, 330°C , tested, not only the calculated lines based on the Eley-Rideal model do not fit well to the experimental data but also the hydrolysis rate is very sensitive to the partial pressure of CS_2 . These phenomena, related to the less hydrophilic behavior of the surface of the titania CRS 31, imply that the CS_2 may become more

competitive on the surface adsorption as compared to water at the condition of higher CS₂ partial pressure and reaction temperatures. It is in a transition state from Eley-Rideal reaction model to Langmuir-Hinshelwood type of reaction model.

5.3.3. Reliability Check of the CS₂ and COS Hydrolysis Rate Equations

For the consecutive reaction (5.5):



the effluent CS₂ and COS compositions from a Berty reactor can be quantitatively described by the following mathematical equations if the independently obtained CS₂ hydrolysis rate function (5.13) and COS hydrolysis rate function (4.20) can well represent the above consecutive reaction at each step.

For the isothermal Berty reactor, the mass conservation equations for CS₂ and COS hydrolysis are:

$$\text{CS}_2: \quad F_t C_{\text{CS}_2}^0 - F_t C_{\text{CS}_2} = W (-r_{\text{CS}_2}) \quad (5.18)$$

$$\text{COS:} \quad F_t C_{\text{COS}} - F_t C_{\text{COS}}^0 = W (-r_{\text{CS}_2}) - W (-r_{\text{COS}}) \quad (5.19)$$

From the ideal gas assumption, we have:

$$C_{\text{CS}_2} = P_{\text{CS}_2} / RT \quad (5.20)$$

$$C_{\text{COS}} = P_{\text{COS}} / RT \quad (5.21)$$

Substitution of equations (4.20), (5.13), (5.20) and (5.21) into equation (5.18) and (5.19) yields:

$$F_t P_{\text{CS}_2}^0 - F_t P_{\text{CS}_2} = RTW \frac{k_1 K_w P_{\text{CS}_2} P_{\text{H}_2\text{O}}}{(1 + K_w P_{\text{H}_2\text{O}})} \quad (5.22)$$

$$F_t P_{\text{COS}} - F_t P_{\text{COS}}^0 = RTW \left\{ \frac{k_1 K_{w1} P_{\text{CS}_2} P_{\text{H}_2\text{O}}}{(1 + K_{w1} P_{\text{H}_2\text{O}})} - \frac{k_2 K_{w2} P_{\text{COS}} P_{\text{H}_2\text{O}}}{(1 + K_{w2} P_{\text{H}_2\text{O}})} \right\} \quad (5.23)$$

Rearrangement of equations (5.22) and (5.23) yields:

$$P_{\text{CS}_2} = \frac{1}{1 + \tau \frac{k_1 K_{w1} P_{\text{H}_2\text{O}}}{1 + K_{w1} P_{\text{H}_2\text{O}}}} P_{\text{CS}_2}^0 \quad (5.24)$$

and

$$P_{\text{COS}} = \frac{\tau k_1 K_{w1} P_{\text{H}_2\text{O}} P_{\text{CS}_2}}{(1 + K_{w1} P_{\text{H}_2\text{O}}) \left(1 + \tau \frac{k_2 K_{w2} P_{\text{H}_2\text{O}}}{1 + K_{w2} P_{\text{H}_2\text{O}}} \right)} + \frac{P_{\text{COS}}^0}{1 + \tau \frac{k_2 K_{w2} P_{\text{H}_2\text{O}}}{1 + K_{w2} P_{\text{H}_2\text{O}}}} \quad (5.25)$$

where $\tau = R \cdot T \cdot W / F_t$.

With equations (5.24) and (5.25), the effluent partial pressure P_{COS} can be predicted for different feed CS_2 partial pressures. A comparison of predicted P_{COS} with experimental observed effluent P_{COS} are shown in Tables 5.4 and 5.5. The predicted COS partial pressure for both Kaiser 201 and CRS 31 is much higher than the observed one. With increasing reaction temperature, the discrepancy becomes larger. Compared to the alumina catalyst (Kaiser 201), titania (CRS 31) shows a much greater discrepancy between the predicted and the observed P_{COS} . In the earlier work done by Akimoto and Dalla Lana (1979), they cautioned that the ratio of rate constant $k_{\text{CS}_2} K_{\text{CS}_2} / k_{\text{COS}} K_{\text{COS}}$ obtained from a co-hydrolysis method (both CS_2 and COS present in the feed) is smaller than that obtained from an initial rate method. In their co-hydrolysis method, the calculation of the ratio of the rate constant was based on the measured global rate of the formation of CO_2 . This method resulted in a low estimate for CS_2 conversion because the measured CO_2 rate was taken as the sum of CS_2 and COS hydrolysis rates. In

Table 5.4 Comparison between Predicted and Measured $P_{\cos}$ (Kaiser 201)

Temperature = 270°C			Temperature = 300°C			Temperature = 330°C		
Exp.	Cal.	Error%	Exp.	Cal.	Error%	Exp.	Cal.	Error%
0.052	0.0846	106.45	0.048	0.0930	93.77	0.041	0.1006	145.51
0.090	0.1309	114.66	0.072	0.1437	99.68	0.061	0.1557	155.40
0.118	0.1724	115.55	0.101	0.1891	87.28	0.080	0.2052	156.57
0.139	0.2091	101.07	0.119	0.2292	92.63	0.104	0.2490	139.44
0.160	0.2362	96.87	0.134	0.2588	93.19	0.120	0.2813	134.45
0.063	0.0991	106.44	0.054	0.1094	92.66	0.048	0.1171	144.09
0.092	0.1279	102.95	0.073	0.1411	93.32	0.063	0.1512	140.00
0.108	0.1646	98.33	0.180	0.3014	67.49	0.083	0.1947	134.58
0.180	0.2733	95.19	0.201	0.3877	92.91	0.140	0.3234	131.04
0.224	0.3516	105.59	0.074	0.1413	91.05	0.171	0.4163	143.48
0.110	0.1646	98.38	0.140	0.2695	92.52	0.083	0.1940	133.81
0.118	0.1918	89.93	0.189	0.3198	69.22	0.101	0.2261	123.86
0.175	0.2446	100.48	0.203	0.3887	91.48	0.122	0.2883	136.32
0.191	0.2893	92.89	0.168	0.3200	90.50	0.150	0.3411	127.40
0.228	0.3517	95.38	0.091	0.1821	100.14	0.180	0.4146	130.34
0.108	0.1647	96.03	0.110	0.2121	92.89	0.084	0.1938	130.72
0.123	0.1918	101.94	0.201	0.3889	93.52	0.095	0.2258	137.69

Table 5.5 Comparison between Predicted and Measured $P_{\cos}$ (CRS 31)

Temperature = 270°C			Temperature = 300°C			Temperature = 330°C		
Exp.	Cal.	Error%	Exp.	Cal.	Error%	Exp.	Cal.	Error%
0.035	0.1267	262.11	0.030	0.1333	344.58	0.028	0.1710	511.05
0.044	0.1659	277.15	0.040	0.1747	336.93	0.031	0.2067	567.08
0.058	0.1985	242.28	0.045	0.2092	365.03	0.040	0.2697	574.48
0.074	0.2538	242.98	0.062	0.2689	333.86	0.047	0.3223	585.92
0.091	0.3063	236.59	0.075	0.3239	331.99	0.018	0.1036	475.73
0.028	0.1030	268.20	0.021	0.1080	414.30	0.034	0.2337	587.36
0.068	0.2299	238.19	0.055	0.2413	338.90	0.045	0.2880	540.11
0.086	0.2822	228.22	0.064	0.2965	363.42	0.052	0.3504	573.84
0.099	0.3409	244.42	0.082	0.3587	337.49	0.058	0.3897	571.92
0.112	0.3778	237.38	0.090	0.3978	342.04	0.021	0.1258	499.28
0.035	0.1295	270.11	0.031	0.1346	334.26	0.043	0.2509	483.53
0.078	0.2578	230.58	0.060	0.2680	346.74	0.058	0.3372	481.45
0.110	0.3461	214.69	0.081	0.3599	344.37	0.069	0.4197	508.33
0.122	0.4303	252.74	0.102	0.4475	338.78	0.082	0.5017	511.89
0.138	0.5136	272.18	0.114	0.5342	368.67	0.038	0.2192	476.90
0.068	0.2274	234.42	0.060	0.2359	293.18	0.046	0.2554	455.30
0.080	0.2649	231.17	0.062	0.2748	343.30	0.053	0.3257	514.70
0.102	0.3377	231.15	0.084	0.3504	317.19	0.069	0.3855	458.70
0.113	0.3995	253.61	0.103	0.4144	302.40	0.083	0.4688	464.83

fact, part of the CS_2 was actually converted to COS. In the initial rate method, the possible interference between CS_2 and COS in the system was excluded. These nearly coincident facts obtained from different experimental methods indicate that the kinetic modelling of the actual hydrolysis mechanism in a CS_2 and COS co-existing system must be more complicated than the one described by the simple consecutive kinetic equation (5.5). Figure 5.7 clearly shows the discrepancy between observed and predicted COS partial pressure.

5.3.4. Reaction Mechanism

The foregoing kinetic studies of CS_2 and COS hydrolysis have glossed over the question of how the CS_2 and COS hydrolysis proceeds on the surface. Based on the fact that the experimentally obtained effluent COS partial pressure is lower than one predicted from the consecutive kinetics equation (5.5), and that the CS_2 and COS hydrolysis rates obey the Eley-Rideal model, a descriptive suggestion for the possible mechanism of CS_2 or COS hydrolysis is shown schematically in Figures 5.8 and 5.9, respectively, in which, the surface of the hydrophilic catalysts (alumina-based Kaiser 201 and titania-based CRS 31) is covered with adsorbed water molecules or OH^- groups. According to the Eley-Rideal model, the CS_2 and COS compounds from the gas phase must interact first with surface H_2O or OH^- to further the reaction. For the highly hydrophilic surface covered with various types of adsorbed water, only a few of the collisions will be effective and lead to the forward reaction according to molecular collision theory. The intermediate compound COS shown in Figure 5.8 is produced from the reaction of gas phase CS_2 with surface H_2O or OH^- group by effective collisions and is most likely bonded to the surface because the reaction must involve the exchange of the S atom from CS_2 molecule with an O atom from the adsorbed H_2O or OH^- group. The bonded COS

Figure 5.7 Change of Effluent COS Partial Pressure Versus Inlet CS_2 Partial Pressure Over the Bertly Reactor

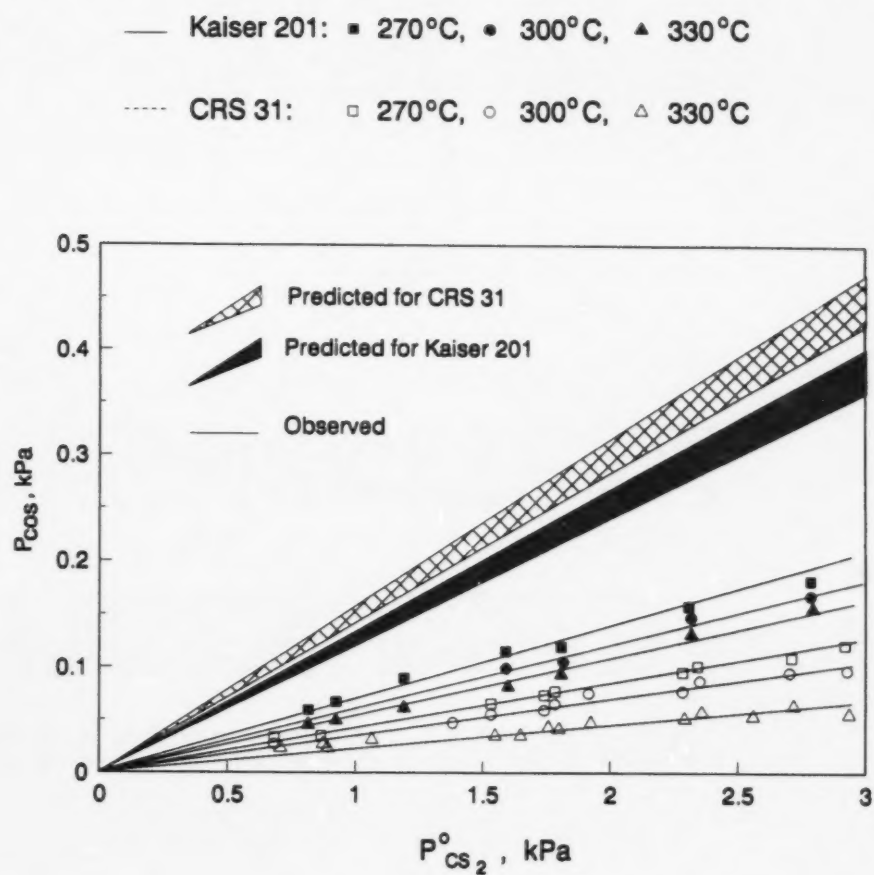


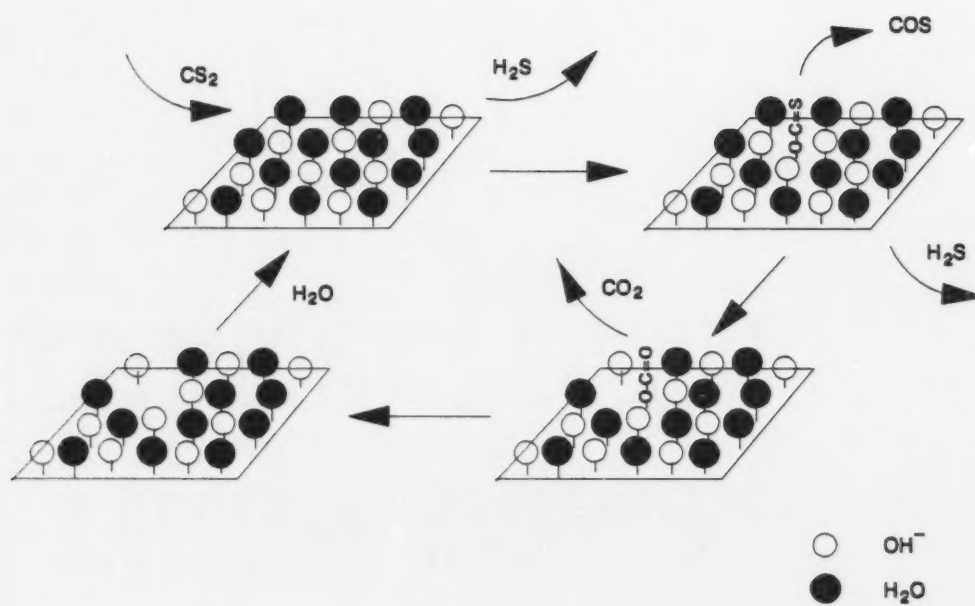
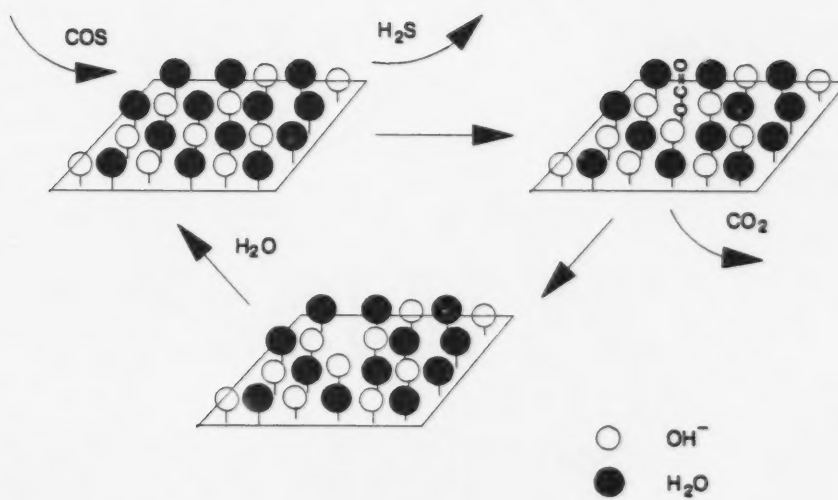
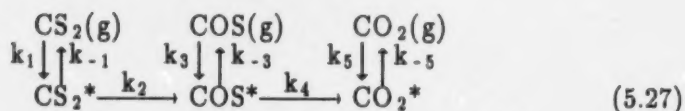
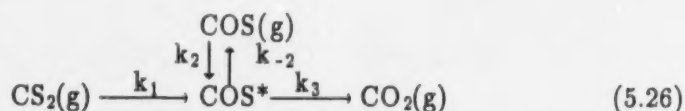
Figure 5.8 Schematic Diagram of CS₂ Hydrolysis Model

Figure 5.9 Schematic Diagram of COS Hydrolysis Model



may be more reactive than the one directly from the gas phase. In the CS₂ hydrolysis experiments, only the part of COS desorbed from the bonded surface was detected in the effluent. Most of the bonded COS was expected to be further hydrolyzed on the surface. Therefore, an effluent COS partial pressure lower than the predicted one was observed in the CS₂ hydrolysis experiments. Since the simple consecutive reaction (5.5) cannot accurately describe the CS₂/COS hydrolysis system, it indicates that the reaction mechanism for the hydrolysis of CS₂ and COS on the catalyst surface must be more complicated. A few other possible reaction networks are proposed. In the following proposed networks, the water role is omitted from the expressions since on these hydrophilic catalysts (Kaiser 201 and CRS 31), water dominantly covers the surface and exhibits zero order behavior in the concentration ranges encountered in the practical situation (10 – 30 mol %).



Compared to consecutive reaction (5.5), the above complex reaction networks (5.26) and (5.27) take surface adsorptions into consideration, being more realistic. Assuming pseudo-first order to CS₂ and COS for the hydrolysis reaction, the corresponding rate expressions to network (5.26) and (5.27) can be obtained as follows:

For reaction network (5.26), assuming pseudo-steady-state for [COS*], we have:

$$\frac{d[\text{COS}^*]}{dt} = k_1 P_{\text{CS}_2} - k_3 [\text{COS}^*] + k_2 P_{\text{COS}} - k_{-2} [\text{COS}^*] = 0 \quad (5.28)$$

or

$$[\text{COS}^*] = \frac{k_1 P_{\text{CS}_2} + k_2 P_{\text{COS}}}{k_3 + k_{-2}} \quad (5.29)$$

The rate expressions are:

$$-r_{\text{CS}_2} = k_1 P_{\text{CS}_2} \quad (5.30)$$

$$-r_{\text{COS}} = k_2 P_{\text{COS}} - k_{-2} [\text{COS}^*] \quad (5.31)$$

Substitution of (5.29) into (5.31) yields:

$$-r_{\text{COS}} = k_2 P_{\text{COS}} - k_{-2} \frac{k_1 P_{\text{CS}_2} + k_2 P_{\text{COS}}}{k_3 + k_{-2}} \quad (5.31)$$

or

$$-r_{\text{COS}} = -\bar{k}_1 P_{\text{COS}} - \bar{k}_2 P_{\text{CS}_2} \quad (5.32)$$

where, $\bar{k}_1 = k_2 k_3 / (k_3 + k_{-2})$ and $\bar{k}_2 = k_1 k_{-2} / (k_3 + k_{-2})$.

For reaction network (5.27), following the same procedure as above, we have:

$$\frac{d[\text{CS}_2^*]}{dt} = k_1 P_{\text{CS}_2} - k_{-1} [\text{CS}_2^*] - k_2 [\text{CS}_2^*] = 0 \quad (5.33)$$

or

$$[\text{CS}_2^*] = \frac{k_1 P_{\text{CS}_2}}{k_{-1} + k_2} \quad (5.34)$$

and

$$\frac{d[\text{COS}^*]}{dt} = k_2 [\text{CS}_2^*] - k_4 [\text{COS}^*] + k_3 P_{\text{COS}} - k_{-3} [\text{COS}^*] = 0 \quad (5.35)$$

or

$$[\text{COS}^*] = \frac{k_2 [\text{CS}_2^*] + k_3 P_{\text{COS}}}{k_4 + k_{-3}} \quad (5.36)$$

Substitution of (5.34) into (5.36) yields:

$$[\text{COS}^*] = \frac{k_1 k_2 / (k_{-1} + k_2) P_{\text{CS}_2} + k_3 P_{\text{COS}}}{k_4 + k_{-3}} \quad (5.37)$$

The rate expressions are:

$$-r_{\text{CS}_2} = k_1 P_{\text{CS}_2} - k_{-1} [\text{CS}_2^*] \quad (5.38)$$

$$-r_{\text{COS}} = k_3 P_{\text{COS}} - k_{-3} [\text{COS}^*] \quad (5.39)$$

Substitution of (5.34) and (5.37) into (5.38) and (5.39) respectively yields:

$$-r_{CS_2} = k_1 P_{CS_2} - k_{-1} \frac{k_1 P_{CS_2}}{k_{-1} + k_2} \quad (5.40)$$

$$\text{or} \quad -r_{CS_2} = \bar{k}_1 P_{CS_2} \quad (5.41)$$

where $\bar{k}_1 = k_1 k_2 / (k_{-1} + k_2)$.

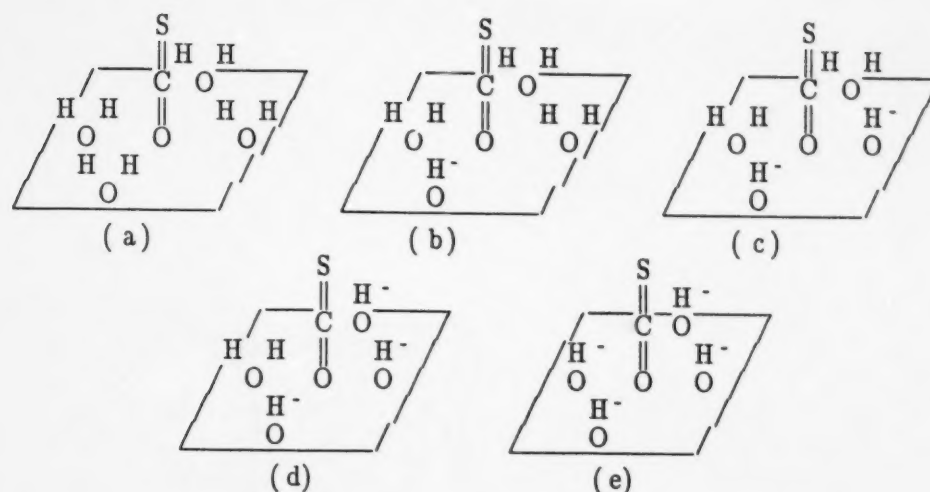
$$-r_{COS} = k_3 P_{COS} - k_{-3} \frac{k_1 k_2 / (k_{-1} + k_2) P_{CS_2} + k_3 P_{COS}}{k_4 + k_{-3}} \quad (5.42)$$

$$\text{or} \quad -r_{COS} = \bar{k}_1 P_{COS} - \bar{k}_2 P_{CS_2} \quad (5.43)$$

where, $\bar{k}_1 = k_3 k_4 / (k_4 + k_{-3})$ and $\bar{k}_2 = k_1 k_2 k_{-3} / (k_{-1} + k_2)(k_4 + k_{-3})$.

From the analysis of kinetic rate expressions for different reaction network shown above, the global rate constants are a group of rate constants representing different reaction paths. The rate constants obtained in our Eley-Rideal model from the independent CS_2 and COS hydrolysis experiments did not consider the reaction path occurring on the surface. The COS produced from CS_2 hydrolysis may appear on the surface first then desorbed to gas phase if not being further hydrolyzed on the surface. But, in the experiments for COS hydrolysis, the COS comes from gas phase first and then may adsorb on the surface to further its reaction with surface water. So either the complication of the CS_2 and COS hydrolysis kinetics or the independent CS_2 and COS hydrolysis experiments create the discrepancy as shown in Figure 5.7. To fully describe the CS_2 and COS co-hydrolysis system, it is necessary to conduct kinetics experiments with both CS_2 and COS in feed and make a more rigorous search for parameters of rate equations by considering the more complicated reaction network like (5.26) and (5.27).

From chemical point of view, for an adsorbed COS^* , there could be various surrounding micro-environments. For example:

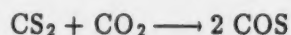


Here, a water molecule could be chemically or physically adsorbed on the solid catalyst surface. If the bonded COS is surrounded by physically adsorbed water as picture (a) shows, the bonded COS may more likely escape to the gas phase instead of furthering the hydrolysis reaction. On the other hand, when the bonded COS is surrounded by chemically adsorbed H_2O or OH^- group as pictures (c), (d) and (e) show, further S/O exchange between bonded COS and surface OH^- group or chemically adsorbed water is more likely because of the more reactive surroundings. The more hydrophilic alumina surface may favor the surface state as picture (a) shows. The surface state in pictures (b), (c) and (d) may be more favorable on the less hydrophilic titania surface. This may be one of the explanations why the titania CRS 31 shows a higher activity and lower COS concentration during the CS_2 hydrolysis reaction than the alumina Kaiser 201. That surface basicity favors the hydrolysis reaction is well known (Luinstra and d'Haene, 1989; Fiedorow et al., 1984; George, 1974). Acid-base properties of the alumina surface have been widely discussed in the literature. During CS_2 and COS hydrolysis reactions, the state of surface water on the catalyst is expected to be

crucial. For the highly hydrophilic alumina-based Kaiser 201, physically adsorbed H_2O may cover a large portion of surface which not only reduces the possibility of breakage of bonded COS but also reduces the fraction of effective collision of gas phase CS_2 and COS with surface active sites. The higher hydrolysis activity and lower COS intermediate concentration in the effluent shown by titania (CRS 31) together with its lower hydrophilicity as compared to alumina (Kaiser 201) indicates that a modification to the alumina surface enabling lower hydrophilicity may be very beneficial for the improvement of its hydrolysis activity.

5.4. CONCLUSIONS

1. The introduction of CO_2 (2 %) or H_2S (2 %) into $CS_2/H_2O/N_2$ feed has no effect on the CS_2 hydrolysis conversion in the ranges of 230 to 340°C tested on either Kaiser 201 or CRS 31. This shows that the appearance of COS in the effluent from CS_2 hydrolysis is not via the synthesis reaction,



but most likely via the consecutive reactions,



2. Intrinsic rate functions for the hydrolysis of CS_2 catalyzed by either alumina (Kaiser 201) or titania (CRS 31) are both best-described by an Eley-Rideal model over the ranges of temperature, 270 to 330°C. The regressed parameters for the rate function

$$-r_{CS_2} = \frac{k_1 K_w P_{CS_2} P_{H_2O}}{(1 + K_w P_{H_2O})}$$

are:

Alumina Kaiser 201:

$$k_1 = \text{Exp}(3.037 - 4.891 \times 10^3/T), \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa})$$

$$K_{w1} = \text{Exp}(-19.49 + 1.184 \times 10^4/T), 1/\text{kPa}$$

$$E = 40.66, \text{ kJ/mol}$$

$$H = 98.44, \text{ kJ/mol}$$

Titania CRS 31:

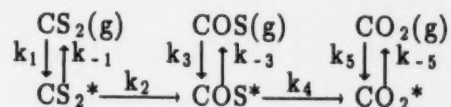
$$k_1 = \text{Exp}(6.786 - 6.813 \times 10^3/T), \text{ mol}/(\text{g} \cdot \text{h} \cdot \text{kPa})$$

$$K_{w1} = \text{Exp}(-25.76 + 1.104 \times 10^4/T), 1/\text{kPa}$$

$$E = 56.64, \text{ kJ/mol}$$

$$H = 91.78, \text{ kJ/mol}$$

3. The reaction kinetics for CS_2/COS hydrolysis on either CRS 31 or Kaiser 201 is not a simple consecutive reaction and is suggested to be described by a complex reaction network, simplified assuming zero-order water behavior,



The fact that the lower concentration of COS intermediate occurs on the titania catalyst CRS 31 during the CS_2 hydrolysis suggests that the highly hydrophilic surface of the alumina catalyst (Kaiser 201) inhibits the consecutive CS_2 and COS hydrolysis.

5.5 NOMENCLATURE

C_{COS}	=	Outlet COS concentration, mol/m^3
C_{CS_2}	=	Outlet CS_2 concentration, mol/m^3
C_{COS}^0	=	Inlet COS concentration, mol/m^3
$C_{\text{CS}_2}^0$	=	Inlet CS_2 concentration, mol/m^3

E	=	Reaction activation energy, kJ/mol
F_t	=	Feed flow rate, m ³ /h.
$k_1, K_{w1}, K_{c1}, K_{d1}$	=	Parameters of the Eley–Rideal or Langmuir–Hinshelwood model function, mol/(g·h·kPa) and 1/kPa.
k_j		Rate constants in reaction network (5.26) and (5.27), $j = 1, -1, 2, -2, 3, -3, 4, 5, -5$.
$\bar{k}_1, \bar{k}_2$		Global rate constants for Equations (5.32), (5.41) and (5.43)
P_{COS}^o	=	Inlet partial pressure of COS, kPa
$P_{\text{CS}_2}^o$	=	Inlet partial pressure of CS ₂ , kPa
P_{COS}	=	Outlet partial pressure of COS, kPa
P_{CS_2}	=	Outlet partial pressure of CS ₂ , kPa
P_t	=	Operation pressure, kPa.
$-r_{\text{CS}_2}$	=	CS ₂ hydrolysis rate, mol/(g·h)
$-r_{\text{COS}}$	=	COS hydrolysis rate, mol/(g·h)
R	=	Gas constant, kJ/(mol·K)
T	=	Absolute temperature, K
W	=	Catalyst weight, g
$(X_{\text{CS}_2})_{\text{in}}$	=	Inlet CS ₂ concentration, mol%
$(X_{\text{CS}_2})_{\text{out}}$	=	Outlet CS ₂ concentration, mol%

Greek Letters

τ	=	Contact time, h·g·kPa/mol
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CHAPTER 6

SIMULATION OF CS_2 AND COS HYDROLYSIS IN A MODIFIED CLAUS PROCESS CONVERTER

6.1. INTRODUCTION

The simulation of the Claus reactor to predict H_2S conversion of the modified Claus process has been pursued by a few authors (Opekar and Goar, 1966; Burns et al., 1974; Cho, 1975 and Razzaghi, 1985). Because of the complexity of the Claus process and experimental difficulties in obtaining some basic data for modelling the Claus process, the simulation model is far from perfect. A few problems which require further consideration in the simulation model are summarized as follows:

1. CS_2 and COS conversions in Claus converter.
2. The kinetics of sulfur vapor equilibrium (S_n , $n = 2, 3, \dots 8$) in the Claus converter.
3. Capillary condensation of sulfur in the catalyst pores.
4. The kinetics of catalyst deactivation by sulfation or carbon fouling.
5. Interaction and competition on surface between CS_2 , COS, H_2S and SO_2

In this part of the work, we would like to extend the simulation model to make it capable of predicting CS_2 and COS conversions in the Claus converter, based on the CS_2 and COS hydrolysis rate functions obtained in Chapters 4 and 5. With the availability of these rate functions, it, in principle, becomes possible to simulate the performance of the Claus converter for CS_2 and COS hydrolysis reactions. However, since the experiments for studying CS_2 and COS kinetics are made independently with no interference from $\text{H}_2\text{S}/\text{SO}_2$ reaction and other poisoning effects like sulfation, carbon deposition and sulfur condensation (which occur in commercial Claus converters), the capability of the simulation model to predict CS_2 and COS conversions in the simulated Claus converter is still limited. To represent the actual Claus converters, catalyst deactivation must also be

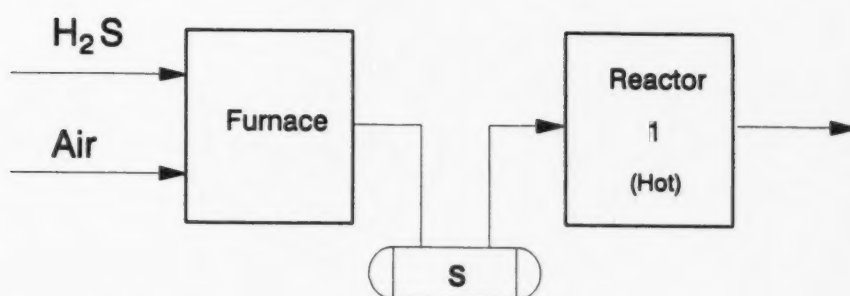
considered. At this stage of our experimental work, a real time-dependent or catalyst surface property related deactivation kinetics model has not yet been obtained. Therefore, to predict the CS_2 and COS conversions in a Claus converter with a partially deactivated Claus catalyst, a simple uniform poisoning model will be used in the following simulation work, assuming that the poisoning degree by sulfation, coking, sulfur accumulation, thermal aging, attrition, etc. in the model can be represented by a percentage of loss of active surface area of the catalyst.

From industrial experience, CS_2 and COS hydrolysis effectively occurs primarily in the first Claus converter within which the reaction temperature is comparatively higher than in the downstream Claus converters. So, our simulation will concentrate on the first Claus converter with an industrial catalyst bed depth of 1 m. Although our kinetic rate equations for CS_2 and COS hydrolysis are obtained independently, the prediction of COS concentrations in a CS_2 and COS co-hydrolysis system using these kinetic rate equations will give conservative results, more so for CRS 31, as Figure 5.7 shows. The predicted COS concentrations will be higher than the actual ones. Figure 6.1 presents a schematic diagram of the simulation of a reactor with the inlet feed composition employed in the computations. A 100 % H_2S gas mixed with the stoichiometric air will comprise the feed to the Claus furnace. Assuming a 70 % conversion of H_2S in the furnace, the effluent from the furnace, after being cooled to condense the sulfur, is taken as feed to the first Claus converter.

6.2 MODEL DEVELOPMENT

The mathematical model for the Claus catalytic reactor developed by Razzaghi (1985) in a program named 'ADONEDIMBED' will be extended to include CS_2 and COS kinetics. The original 'ADONEDIMBED' program was

Figure 6.1 Simulation of Reactor (inlet feed compositions)



mol %	Feed to Furnace	Feed to First Converter
H_2S	32	7
SO_2	-	3.5
N_2	53.71	64.32
O_2	14.3	-
H_2O	-	25.0
CS_2	-	0.08
COS	-	0.1

limited to predicting the performance of a Claus converter for Claus reaction only and was developed according to the scheme of Table 6.1.

Table 6.1 Scheme for Development of Models for High Temperature
Claus Converter

Chemical changes	adsorption/reaction/desorption
Transport processes inside the catalyst pellets	heat/mass
Transport processes in a film layer	heat/mass
Interaction with environment	adiabatic, 1-dimensional, ideal gas behavior and S_n species instantaneously equilibrate
Catalyst	alumina, Kaiser 201/no deactivation
Numerical method	Runge-Kutta-Fehlberg and Newton-Raphson schemes

For the adiabatic, 1-dimensional model, the major computations involve a material balance for component, C_{fj} :

$$\frac{d(V_s C_{fj})}{dz} + a_m k_{mj} (C_{fj} - C_{sj}) = 0 \quad (6.1)$$

$$j = 1, 2, 3$$

and heat balance for the fluid phase

$$\frac{d(V_s \rho T_f)}{dz} - \left(\frac{a_m \cdot h}{C_p}\right)(T_s - T_f) = 0 \quad (6.2)$$

with the coupling equations between catalyst and fluid phases,

$$a_m k_{mj} (C_{fj} - C_{sj}) = -a_j \rho \eta (R_s) \quad (6.3)$$

$$a_m \cdot h (T_s - T_f) = (-\Delta H) \rho \eta (R_s) \quad (6.4)$$

and for conservation of the various sulfur species,

$$\frac{d(V_s Z_f)}{dz} + a_m k_{m6} (Z_f - Z_s) = 0 \quad (6.5)$$

$$a_m k_{m6} (Z_f - Z_s) = -6a_6 \rho \eta R_s \quad (6.6)$$

where, $Z = 2 C_{S2} + 4 C_{S4} + 6 C_{S6} + 8 C_{S8} \quad (6.7)$

Equation (6.6) is based on S_6 species.

To predict CS_2 and COS hydrolysis conversions in the Claus converter, the following two mass balance equations for describing an adiabatic, 1-dimensional reactor must be included in the analysis:

$$\frac{d(V_s C_{fi})}{dz} + a_m k_{mi} (C_{fi} - C_{si}) = 0 \quad (6.8)$$

$$a_m k_{mi} (C_{fi} - C_{si}) = \rho \eta_i (-r_i) \quad (6.9)$$

where, $i = CS_2, COS$

Since the modelling of CS_2 and COS hydrolysis in the Claus converter is an extension of the adiabatic 1-dimensional model developed by Razzaghi (1985), all the assumptions shown in Table 6.1 are used for the computations of CS_2 and COS hydrolysis conversions. The heat contributions from CS_2 and COS hydrolysis are neglected in the energy conservation equation (6.4) to simplify the numerical computations in the computer program. Since the concentration of CS_2/COS in the feed as shown in Figure 6.1 is much lower than that of H_2S/SO_2 and the heat of reaction for CS_2 and COS hydrolysis is smaller than that for the reaction of H_2S with SO_2 within the temperature range shown in Table 6.2, neglecting reaction heat from hydrolysis reactions will not introduce a noticeable deviation from the temperature profile predicted by solely considering the heat of Claus reaction. An estimation of reaction heat based on Equation (6.10) shows that for the feed

composition to Claus first converter listed in Table 6.1, a 100 % conversion for CS_2 and COS hydrolysis reaction will produce only about 1/70 to 1/82 of heat as produced by the 100 % conversion of H_2S .

$$\text{Heat Ratio} = \frac{X_{\text{CS}_2} \Delta H(\text{for } \text{CS}_2 \text{ hydrolysis}) + X_{\text{COS}} \Delta H(\text{for COS hydrolysis})}{X_{\text{H}_2\text{S}} \Delta H(\text{for Claus reaction})} \quad (6.10)$$

where X_{CS_2} , X_{COS} and $X_{\text{H}_2\text{S}}$ are mol % of CS_2 , COS and H_2S in feed.

Table 6.2 Reaction Heat (kJ) for the Claus and the Hydrolysis Reactions

Reaction	227°C	327°C	427°C
$\text{CS}_2 + \text{H}_2\text{O} = \text{COS} + \text{H}_2\text{S}$	-34.54	-34.66	-34.69
$\text{COS} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2\text{S}$	-34.42	-34.61	-34.69
$2\text{H}_2\text{S} + \text{SO}_2 = 1/2\text{S}_8 + \text{H}_2\text{O}$	-92.00	-90.94	-90.14
$2\text{H}_2\text{S} + \text{SO}_2 = 3/16\text{S}_8 + \text{H}_2\text{O}$	-104.88	-103.60	-102.6

CS_2 and COS hydrolysis rates appearing in equation (6.9) are described by an Eley-Rideal model as follows:

$$-r_i = \frac{k_i K_{wi} C_{\text{H}_2\text{O}} C_{si}}{(1 + K_{wi} C_{\text{H}_2\text{O}})} \quad (6.11)$$

where, $i = \text{CS}_2$ or COS

When the condition of $K_{wi} C_{\text{H}_2\text{O}} \gg 1$ is satisfied, equation (6.11) simplifies to a pseudo-first-order rate equation,

$$-r_i = k_i C_{si} \quad (6.12)$$

where, $i = \text{CS}_2, \text{COS}$.

Solving for C_{si} from equations (6.9) and (6.12) yields:

$$C_{si} = \frac{a_m k_{mi}}{a_m k_{mi} + \rho \eta_i k_i} \quad (6.13)$$

Substitution of (6.13) into (6.8) and rearrangement yields:

$$\frac{d(V_s C_{fi})}{dz} + \frac{1}{\frac{1}{a_m k_{mi}} + \frac{1}{\rho \eta_i k_i}} C_{fi} = 0 \quad (6.14)$$

By integrating equation (6.14) between the limits of $z=0$ and $z=z$ along the bed, together with equations (6.1) to (6.6), the profile of C_{fi} along the bed can be predicted, and, as a result, the conversion of CS_2 and COS hydrolysis can be calculated by equation (6.15):

$$\text{Conv. \%} = \frac{Q_o C_o - Q_e C_e}{Q_o C_o} \quad (6.15)$$

6.3. NUMERICAL RESULTS FOR NON-DEACTIVATED CATALYST KAISER 201 IN A SIMULATED CLAUS CONVERTER

Figure 6.2 shows that the temperature profile along the bed axis eventually approaches a constant temperature at equilibrium conversion. Increasing the inlet feed temperature increases the asymptotic maximum temperature approached because of the thermodynamic limitation for the reversible Claus reaction. Figure 6.3 shows the effect of the feed temperature on the H_2S conversion profile along the reactor with a constant space velocity of 1000 h^{-1} . A conversion of 83 % was attained in the simulated 1 m deep catalyst bed using a feed temperature of 230°C . When the inlet feed temperature increased to 330°C , the attainable maximum conversion decreased to 72 % at the catalyst bed depth of 0.5 m. In this case, more than 50 % of the bed served no catalytic function in the conversion of H_2S to sulfur. If the inlet feed temperature was increased further, the attainable H_2S

Figure 6.2 Temperature Profile Along the Catalyst Bed Depth

Simulation Condition for the One-Dimensional Adiabatic Reactor:

Inlet Temperature = 230 to 330°C, Pressure = 1.0 atm.

Space Velocity = 1000 hr⁻¹.

Inlet Composition, mol %:

H₂S = 7.0, SO₂ = 3.5, H₂O = 25.0, N₂ = 64.5

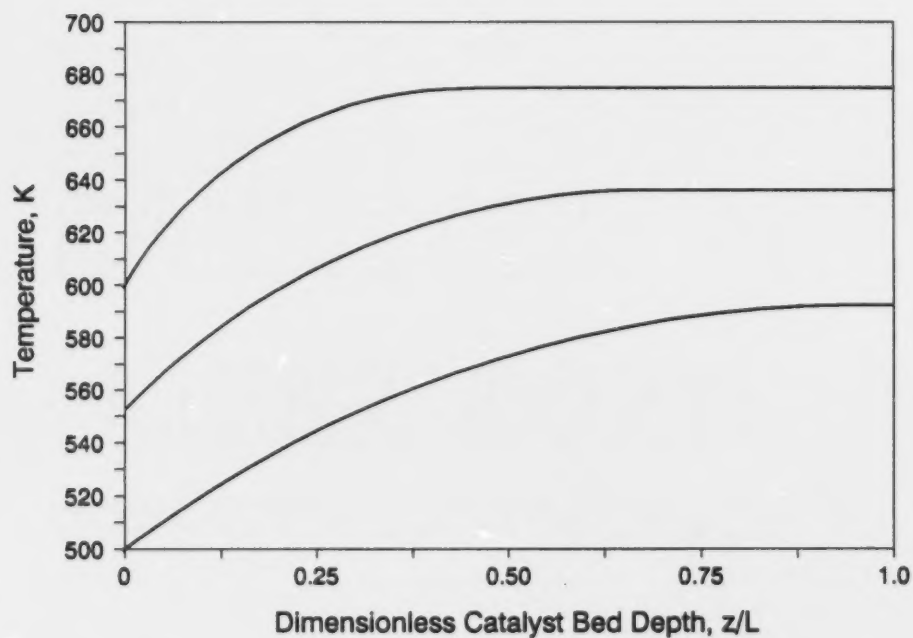


Figure 6.3 Effect of Inlet Temperature on the Performance of the Claus Converter
for H_2S Conversion

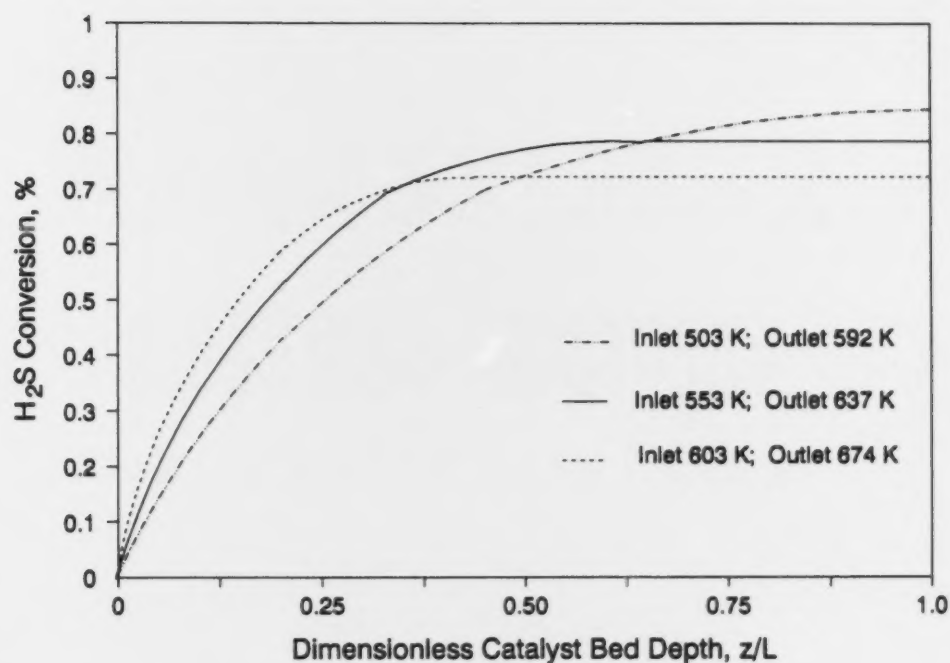
Simulation condition for the One-Dimensional Adiabatic Reactor:

Inlet Temperature = 230 to 330°C, Pressure = 1.0 atm.

Space Velocity = 1000 hr^{-1} .

Inlet Composition, mol %:

H_2S = 7.0, SO_2 = 3.5, H_2O = 25.0, N_2 = 64.5



conversion also decreased with even less of the catalytic bed contributing to the Claus reaction. This suggests that the feed inlet temperature is a very significant factor for the conversion of H_2S in the Claus converter. However, as Figure 6.4 shows, for simultaneous CS_2 and COS hydrolysis reactions in the same simulated Claus converter, the conversion continuously increases along the bed without equilibrium limitation. A conversion exceeding 90 % was predicted with the feed temperature of 230°C . When the feed temperature is increased, the CS_2 and COS conversions are increased too, unlike H_2S conversion which decreases with the increase of feed temperature. Since the temperature in Claus first converter is the highest as compared to the downstream Claus converters, the CS_2 and COS conversions are higher. In the following Claus converters, the reactor temperature has to be decreased to increase the $\text{H}_2\text{S}/\text{SO}_2$ conversion, which will decrease the conversion of CS_2 and COS . This simulation result indicates that the non-deactivated alumina catalyst (Kaiser 201) can generate a high conversion for CS_2 and COS hydrolysis in the Claus first converter. The high feed temperature limits $\text{H}_2\text{S}/\text{SO}_2$ conversion to a lower level but favors CS_2 and COS hydrolysis conversions.

6.4. NUMERICAL RESULTS FOR PARTIALLY DEACTIVATED CATALYST (KAISER 201) IN A SIMULATED CLAUS CONVERTER

As mentioned before, commercial catalysts in the Claus process will experience a certain degree of deactivation. In the first Claus converter, sulfation is regarded as the major deactivating effect on the CS_2 and COS hydrolysis (sulfur, 1990; Pearson, 1981; Kerr, 1977). From plant experience, a moderate-aged alumina catalyst exhibits only 50 to 60 % conversion for CS_2 and COS hydrolysis and requires a higher temperature (for example: 350°C) to reach a 90 %

Figure 6.4 Effect of Feed Temperature on Simultaneous Claus and Hydrolysis Conversions.

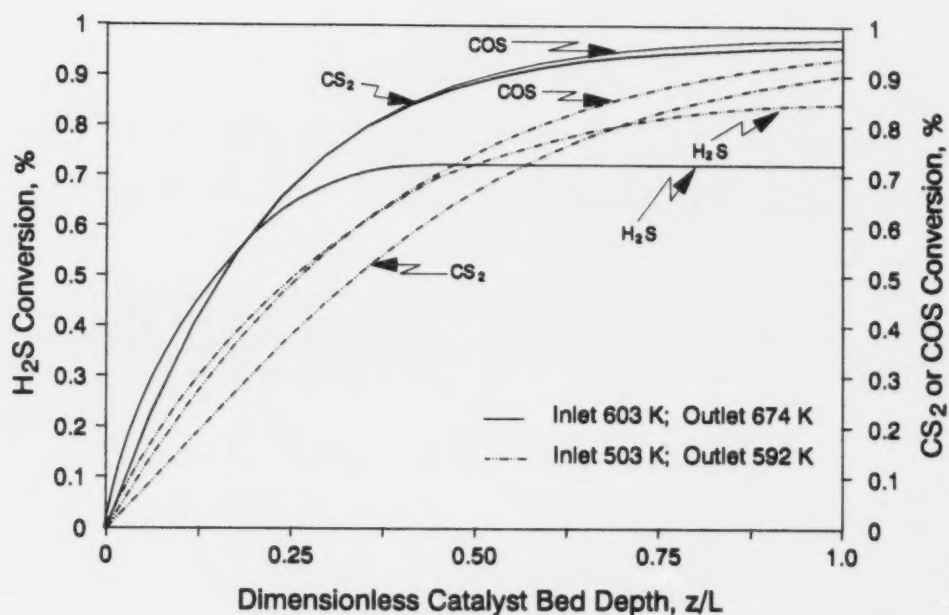
Simulation Condition for the One-Dimensional Adiabatic Reactor:

Inlet Temperature = 230 or 330°C, Pressure = 1.0 atm.

Space Velocity = 1000 hr⁻¹, Catalyst: Kaiser 201

Inlet Composition, mol %:

H₂S = 7.0, SO₂ = 3.5, H₂O = 25.0, CS₂ = 0.08%, COS = 0.1, N₂ = 64.32.



conversion. Figure 6.5 presents the simulation of the sulfation poisoning of CS_2 and COS conversions, using the percentage loss of the initial active surface to represent the degree of sulfation. For a feed temperature of 230°C , the alumina catalyst simulated with 50 to 60 % conversion for CS_2 and COS hydrolysis corresponds to 90 % of the catalyst surface being sulfated. With this degree of sulfation, the simulation results shown in Figure 6.6 predict that an increase of feed temperature to 350°C is required to elevate CS_2 and COS conversions to over 84 %. However, the increase in feed temperature, as predicted in Figure 6.3, would greatly reduce the conversion of H_2S for the Claus reaction. For example, a 330°C inlet feed temperature limited the Claus conversion to 73 % with 50 % of the bed serving no function for the H_2S conversion. The increase in feed temperature may be economically unfavorable. Extending the length of the catalyst bed may elevate CS_2 and COS conversions but would not increase the Claus conversion due to equilibrium limitation.

6.5. METHODS TO INCREASE CS_2 AND COS CONVERSION WITHOUT INCREASING FEED TEMPERATURE

Catalyst deactivation occurs in the Claus converter. As the above simulated results show, a 60 % conversion of CS_2/COS hydrolysis resulted from a 90 % loss of catalyst active surface area. Practical experience together with these simulated results have shown that a higher reaction temperature can elevate CS_2 and COS conversions. But, as discussed in section 6.3, a higher temperature limits the conversion of $\text{H}_2\text{S}/\text{SO}_2$. So the improvement of CS_2 and COS conversions remains to be pursued by methods other than increasing feed temperature. Modification of the catalyst surface to increase its activity to CS_2 and COS

Figure 6.5 Sulfation Effect on CS₂ and COS Conversions

Simulation Condition for the One-Dimensional Adiabatic Reactor:

Inlet Temperature = 230°C, Pressure = 1.0 atm.

Space Velocity = 1000 hr⁻¹, Catalyst Kaiser 201

Inlet Composition, mol %:

H₂S = 7.0, SO₂ = 3.5, H₂O = 25.0, CS₂ = 0.08%, COS = 0.1, N₂ = 64.32.

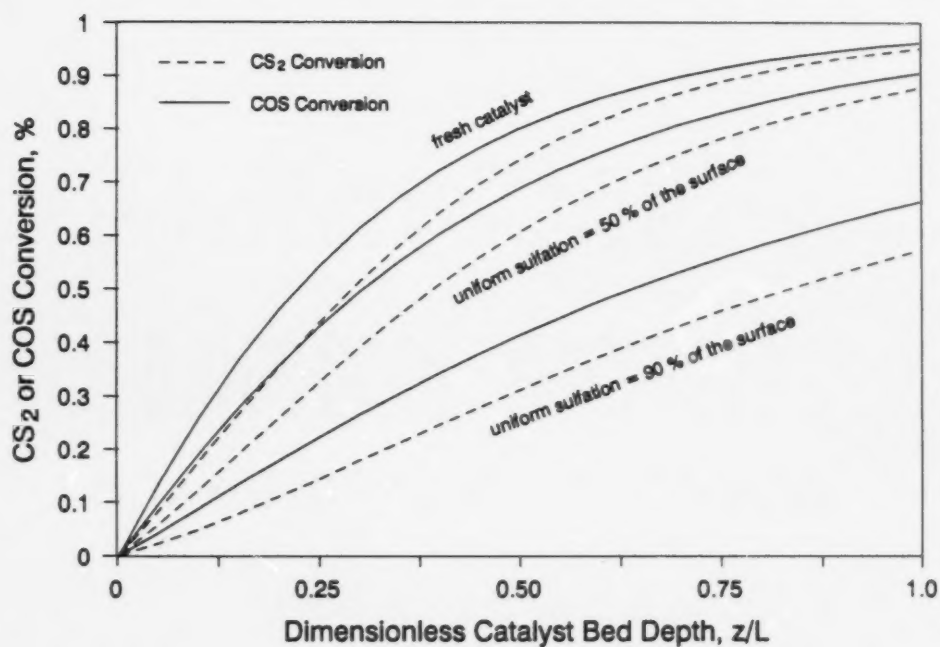


Figure 6.6 Effect of Feed Temperature on CS_2 and COS Conversions for a 90 % Sulfated Catalyst

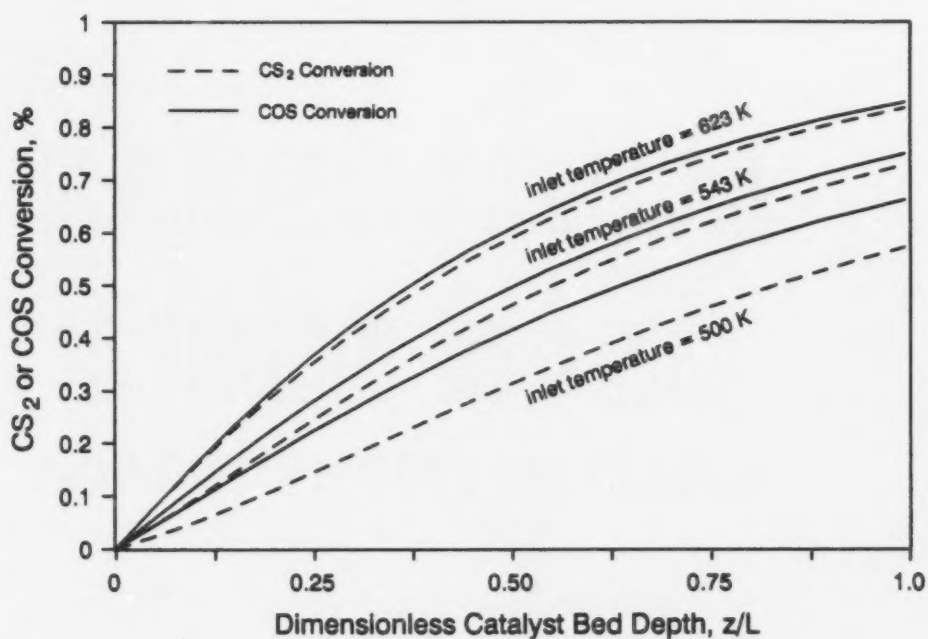
Simulation Condition for the One-Dimensional Adiabatic Reactor:

Inlet Temperature = 230°C , Pressure = 1.0 atm.

Space Velocity = 1000 hr^{-1} , Catalyst: Kaiser 201 with 90 % surface sulfated

Inlet Composition, mol %:

$\text{H}_2\text{S} = 7.0$, $\text{SO}_2 = 3.5$, $\text{H}_2\text{O} = 25.0$, $\text{CS}_2 = 0.08\%$, $\text{COS} = 0.1$, $\text{N}_2 = 64.32$.



hydrolysis is one of the alternatives but this requires much experimental work to find a proper catalytic material. Another alternative may result from changing the catalyst geometry to improve gas diffusion efficiency. The change of catalyst geometry can alter the value of the Thiele modulus which is defined by equation (6.16) for first order kinetics:

$$\phi_i = L_p \sqrt{k_i/D_e} \quad (6.16)$$

where L_p is Aris' (1957) characteristic size defined by equation (6.17):

$$L_p = V_p/S_p = \frac{\text{volume of catalyst particle}}{\text{outer surface of the particle}} \quad (6.17)$$

The value of the Thiele modulus influences the catalyst effectiveness factor somewhat inversely,

$$\eta_i = \frac{1}{\phi_i} \left(\frac{1}{\tanh(3\phi_i)} - \frac{1}{3\phi_i} \right) \quad (6.18)$$

A smaller L_p value results in a larger catalyst effectiveness factor and therefore should increase the catalyst efficiency for CS_2 and COS conversions. Figure 6.7 shows some selected forms of catalyst geometry with different L_p values. Figure 6.8 presents simulated results for an 90 % deactivated alumina catalyst (Kaiser 201) with different geometry, showing that the catalyst with $L_p = 0.022$ cm can elevate CS_2/COS global conversion to 100 %, compared to a 70 % conversion for its spherical shape ($L_p = 0.1$ cm). The reason for this improvement is that, for a diffusion-controlled reaction, an increase in the catalyst's outer surface (S_p) increases gas phase molecule transport passage into the inner surface of the catalyst. When a catalyst is severely deactivated, the reduction of molecular diffusion resistance becomes significant in enabling more efficient use of the small fraction of undeactivated internal surface. Although a change in physical

Figure 6.7 Selected Forms of Catalyst Particles With Different Characteristic Sizes

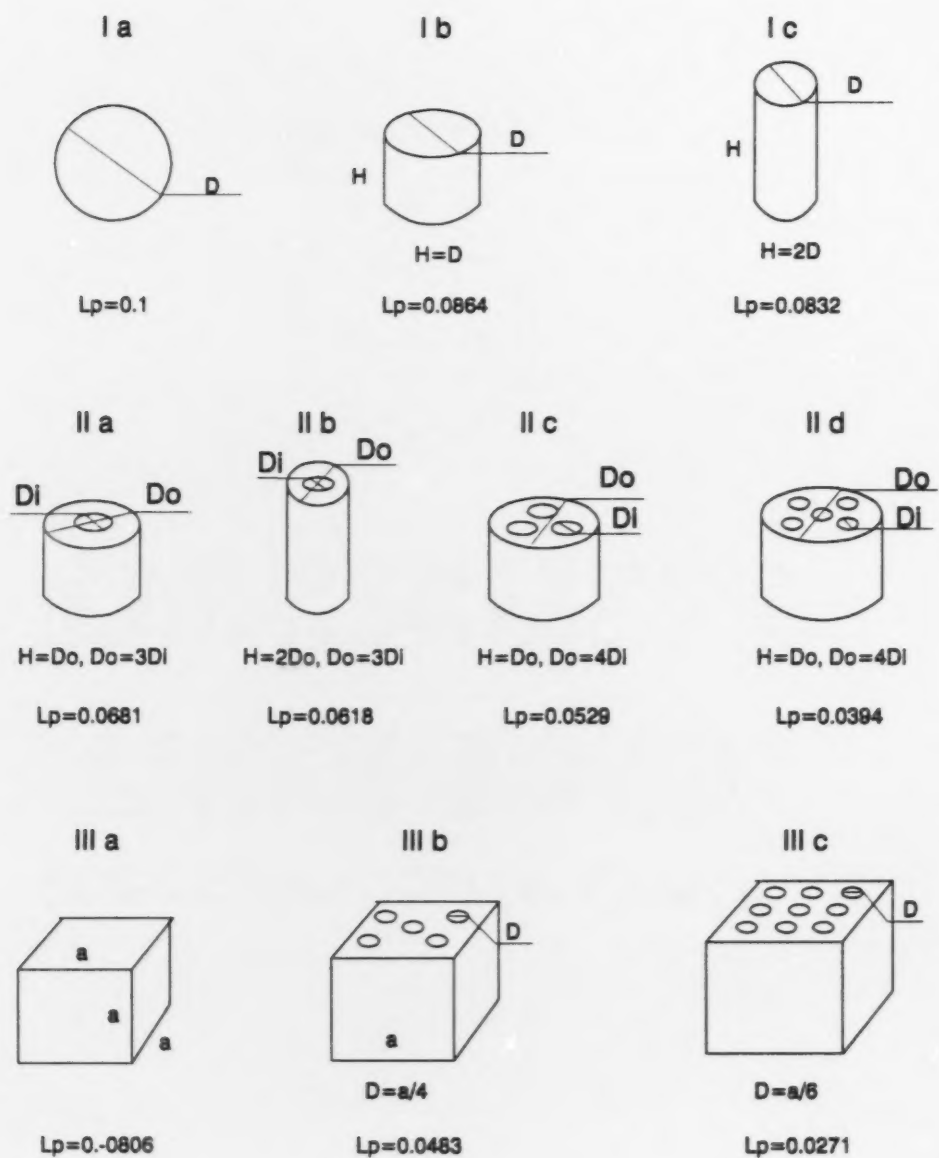


Figure 6.8 Effect of Catalyst Geometry on CS_2 and COS Conversions in a Simulated Claus Converter with a Partially Deactivated Catalyst Bed

Simulation Condition for the One-Dimensional Adiabatic Reactor:

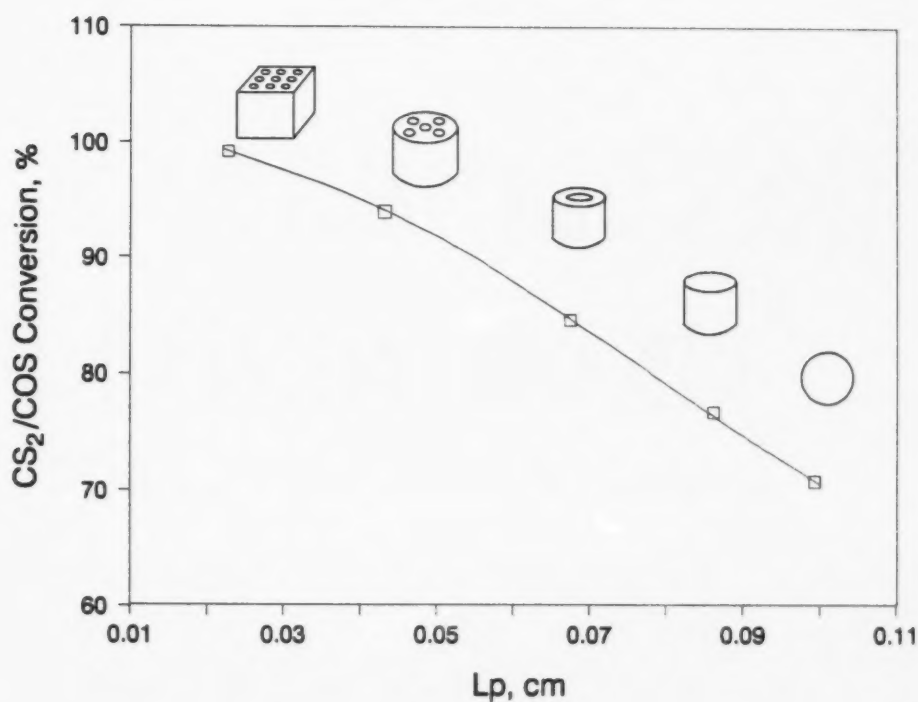
Inlet Temperature = 230°C , Pressure = 1.0 atm.

Space Velocity = 1000 hr^{-1} .

Inlet Composition, mol %:

$\text{H}_2\text{S} = 7.0$, $\text{SO}_2 = 3.5$, $\text{H}_2\text{O} = 25.0$, $\text{CS}_2 = 0.08\%$, $\text{COS} = 0.1$, $\text{N}_2 = 64.32$.

Deactivated Degree: 90 % loss of activity with uniform poisoning



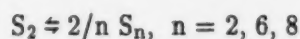
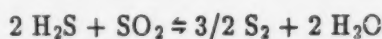
geometry of the catalyst cannot stop catalyst deactivation with time, it increases the catalyst efficiency. This may be an additional contributing reason why the more efficient CRS 31 catalyst on the market uses cylindrical geometry.

6.6 CONCLUSIONS

1. By using an adiabatic one-dimensional simulation of a modified Claus process catalytic converter, with simultaneous kinetics for the consecutive hydrolysis reactions:



and for the Claus reaction:



the CS_2 and COS conversions attainable in an industrial Claus converter were estimated for the alumina catalyst (Kaiser 201). The results indicated that for the non-deactivated alumina catalyst (Kaiser 201), CS_2 and COS conversions exceeding 90 % could be obtained in a simulated commercial Claus converter when the feed temperature is above 230°C.

2. When catalyst deactivation was considered, the "Uniform Poisoning Model" applied to a catalyst with 90 % loss of activity for CS_2 and COS hydrolysis predicted that for a moderate-aged alumina catalyst, 56 % conversion of CS_2 and 65 % conversion of COS may be expected. Increasing the operating temperature can increase CS_2 and COS conversion, but reduces the conversion of the Claus reaction. Extension of the catalyst bed may also increase CS_2 and COS conversion, but it is not beneficial to additional

Claus conversion.

3. Catalyst geometry with a large ratio of S_p/V_p has a positive effect on the conversion of CS_2 and COS hydrolysis. As predicted, for the 90 % deactivated alumina catalyst (Kaiser 201), the catalyst with a hollow cylindrical geometry can attain 85 % conversion of CS_2 and COS instead of 70 % as is the case with a spherical shape. But this modification of catalyst geometry, though good for CS_2 and COS hydrolysis, is not beneficial to the conversion for H_2S/SO_2 reaction because of the thermodynamic limitation.
4. The simulation of kinetics of simultaneous reactions on a catalyst surface is a complex problem. Our Eley-Rideal model, which failed to predict COS concentration in the CS_2 hydrolysis experiments, offers conservative predictions of the performance of the Claus converter for the hydrolysis of CS_2 and COS. Additional kinetics factors which may affect the accuracy of our simulation work include:
 - a. possible competition from H_2S and SO_2 for same sites on the surface involved in the hydrolysis reactions;
 - b. capillary condensation of sulfur which may reduce the catalytic surface area;
 - c. the possibility that the Eley-Rideal model may not be the best basis for intrinsic kinetics.

6.7 NOMENCLATURE

a_j = Stoichiometric coefficient of species, j

a	=	Effective film transfer area, m^2/m^3
C_e	=	Outlet concentration of CS_2 , mol/m^3
C_f	=	Bulk fluid concentration, mol/m^3
C_o	=	Inlet concentration of CS_2 , mol/m^3
C_p	=	Fluid specific heat capacity, $\text{J}/(\text{mol} \cdot \text{K})$
C_s	=	Catalyst surface concentration, mol/m^3
$-\Delta H$	=	Heat of reaction, J/mol
D_e	=	Effective diffusivity, m/s .
F_t	=	Feed flowrate, m^3/s .
h	=	Film heat transfer coefficient, $\text{W}/(\text{m}^2 \cdot \text{s})$
k_i	=	First-order rate constant, $\text{mol}/(\text{g} \cdot \text{s} \cdot \text{atm})$, $i = \text{CS}_2, \text{COS}$
k_m	=	Film mass transfer coefficient, m/s
L	=	Total depth of the catalyst bed, m
L_p	=	V_p/S_p , ratio of particle volume over outside surface area, m .
P_{CS_2}	=	Partial pressure of CS_2 , P_a
P_{COS}	=	Partial pressure of COS , P_a
P_t	=	Operation pressure, P_a
Q_o	=	Inlet gas flowrate, m^3/s
Q_e	=	Outlet gas flowrate, m^3/s
$-r_i$	=	Reaction rate, $\text{mol}/(\text{g} \cdot \text{s} \cdot P_a)$, $i = \text{CS}_2, \text{COS}$
$-r_{\text{CS}_2}$	=	CS_2 hydrolysis rate, $\text{mol}/(\text{g} \cdot \text{s} \cdot P_a)$
$-r_{\text{COS}}$	=	COS hydrolysis rate, $\text{mol}/(\text{g} \cdot \text{s} \cdot P_a)$
R_s	=	Reaction rate of Claus reaction, $\text{mol}/(\text{g} \cdot \text{s} \cdot P_a)$
R	=	Catalyst radius, m
S_p	=	Catalyst outer surface area, m^2
T_f	=	Fluid temperature, K

T_s	=	Catalyst Temperature, K
V_p	=	Catalyst volume, m^3
V_s	=	Superficial velocity, m/s
z	=	Axial position, m
Z	=	Parameter defined by equation (6.7)

Greek Letters

ρ	=	Catalyst particle Density, g/m^3
η	=	Catalyst effectiveness factor.
ϕ	=	Thiele Number

Subscripts

1	=	H_2S
2	=	SO_2
3	=	H_2O
4	=	S_2
5	=	S_4
6	=	S_6
7	=	S_8
8	=	inert
i	=	CS_2 or COS
j	=	1, 2, 3, 4, 5, 6, 7, 8

6.8 BIBLIOGRAPHY

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CHAPTER 7

CS₂ HYDROLYSIS ON PROMOTED ALUMINA CATALYSTS

7.1 INTRODUCTION

In our previous work, the activity of alumina (Kaiser 201) for CS_2 and COS hydrolysis was found to be inferior to that of titania (CRS 31). However, based on the measured CS_2 and COS kinetics, the attainable conversion of CS_2/COS hydrolysis in a simulated commercial Claus converter was still satisfactorily high (>90%). The real problem with the alumina catalyst (with its lower CS_2 and COS conversions in the practical Claus converter) appears to be its susceptibility to deactivation. For example, sulfation happens if the conditions in the plant reactor accidentally become oxidizing. Using an alumina particle of improved geometry may help to compensate for the loss of CS_2/COS conversion due to catalyst deactivation up to a certain degree, as indicated in the simulated reactor performances in Chapter 6, but this certainly cannot prevent catalyst deactivation. An efficient solution would be to find a catalyst more resistant to deactivation. For example, the addition of a suitable promoting agent to alumina may be helpful. Such a dual-function catalyst, which might catalyze CS_2 and COS hydrolysis in the Claus converter side-by-side with the main Claus reaction, would be useful. This part of the work is to test some catalytic materials for the above purposes.

7.2 EXPERIMENTAL METHODS

7.2.1 Preparation of Catalysts

Activated alumina was purchased from Alcoa Chemicals. The chemicals used as additives, ferric nitrate, cupric nitrate, zinc acetate and sodium acetate, were all A.R. grade (BDH chemicals; Fisher Scientific Company).

The activated alumina was ground to -25+30 mesh and was then impregnated to incipient wetness with an aqueous solution containing one of the

above chemicals for each catalyst. An equivalent volume amount impregnation method was used to load metal ion on the alumina support. The saturated particles were kept overnight at room temperature, dried at 120°C for two hours and then calcinated at 400°C for eight hours. Four promoted catalysts, Fe/Al₂O₃, Cu/Al₂O₃, Zn/Al₂O₃ and Na/Al₂O₃, in their oxidized forms, were prepared and their catalyst compositions are listed in Table 7.1. The 5 % by wt composition of the Cu/Al₂O₃ was chosen as the basis for comparison based on the earlier work done by Cho (1975), in which the surface of the alumina catalyst was covered with an approximate one layer of doped metal atom.

Table 7.1 Promoted Catalysts and Their Compositions

Catalyst	Metal wt %	Metal Mol %
Iron-Alumina	4.417	7.785
Copper-Alumina	5.006	7.787
Zinc-Alumina	5.137	7.787
Sodium-Alumina	1.869	7.787

7.2.2 Reactants and Apparatus

The reactants, CS₂ and H₂O, and the Berty reactor—chromatography reaction system used were described in Chapter 2. The conversion of CS₂ was calculated on the basis of the material balance of CS₂ by

$$\% \text{ Conversion of CS}_2 = 100 (C_o - C_e)/C_o \quad (7.1)$$

Preliminary experiments with an empty reactor showed that the reactor itself did not promote CS₂ hydrolysis. The testing and comparing of these promoted catalysts were based on 2.0 g of -25+30 mesh size particles loaded in the Berty reactor. The feed CS₂ and H₂O concentration were 1 mol % and 4 mol %

respectively. The promoted catalysts and the alumina catalyst (Kaiser 201) were tested directly under the $\text{CS}_2/\text{H}_2\text{O}/\text{N}_2$ feed stream first and then tested under $\text{CS}_2/\text{H}_2\text{O}/\text{H}_2\text{S}/\text{N}_2$ feed stream following a standard operating procedure described in the next section.

7.2.3 Operating Procedure

Under a small nitrogen flow, the reactor was heated to the reaction temperature to be tested. Then the nitrogen was replaced by the feed mixture ($\text{CS}_2/\text{H}_2\text{O}/\text{N}_2$). The collection of experimental data was initiated after five hours of reaction. The CS_2 concentration from the outlet of the reactor was analyzed by GC every half an hour until it became constant. After completion of CS_2 hydrolysis testing over a range of temperatures (230 to 340°C), H_2S (2 mol %) was introduced with the feed. After another five hours of reaction, the CS_2 conversion was measured again over the same range of temperatures. The purpose of introducing H_2S into the feed was to study the effect of H_2S gas (reducing agent) on the metal oxide doped on the alumina catalyst and its influence upon the activity of the catalyst.

7.3 RESULTS AND DISCUSSION

7.3.1 Catalyst Activity

Under the standard conditions of 1 mol % CS_2 , 4 mol % H_2O with or without H_2S introduced, the conversions of CS_2 hydrolysis on each catalyst were measured over the range of temperatures from 230 to 340°C. As shown in Figure 7.1, all of the transition-metal-doped catalysts exhibit higher activity for CS_2 hydrolysis than the alumina catalyst (Kaiser 201). When H_2S was introduced with the feed, the activity of transition-metal-doped catalysts for the conversion of CS_2

Figure 7.1 Catalytic Activity of Promoted Catalysts

Test Conditions:

Pressure = 150 kPa, Total Flowrate = 0.03 m³/h

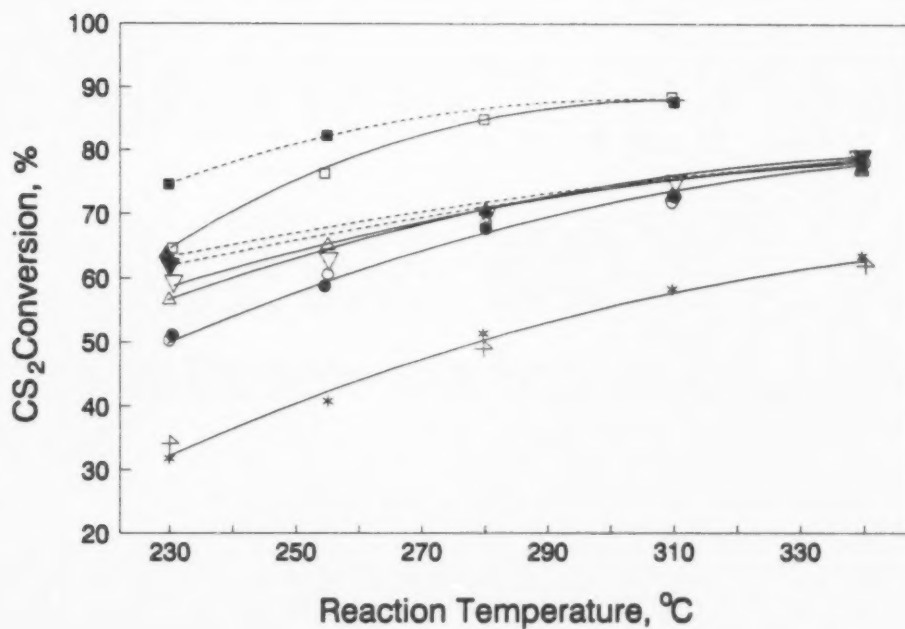
Feed Composition, mol %:

CS₂ = 1.0, H₂O = 4.0, N₂ = 95.0or CS₂ = 1.0, H₂O = 4.0, H₂S = 2.0, N₂ = 93.0Before Adding H₂S

- * Na/Alumina
- ▽ Zn/Alumina
- △ Cu/Alumina
- Fe/Alumina
- Kaiser 201

After Adding H₂S

- ⊕ Na/Alumina
- ▼ Zn/Alumina
- ▲ Cu/Alumina
- Fe/Alumina
- Kaiser 201



was enhanced, exhibiting some increase in CS_2 conversion at the lower temperatures tested, compared to the activity of the catalyst without introducing H_2S . This suggests that H_2S appears to be an activating agent. However, this activating action diminished with the increase of temperature and disappeared at 340°C . Among the catalysts tested, the iron-doped alumina catalyst exhibited the highest activity for CS_2 hydrolysis. Comparison to Figure 3.6, which showed that bauxite exhibited the highest catalytic activity below 290°C , suggests that the iron content of bauxite may be beneficial in promoting CS_2 hydrolysis. The introduction of H_2S gas into the reactant feed had no effect on the activity of either the sodium-doped alumina catalyst or the alumina Kaiser 201, unlike the transition-metal-doped catalysts.

7.3.2 Catalyst Surface

The difference in CS_2 hydrolysis activity before and after introducing H_2S into the reactor was found to be due to the sulfiding of the doped transition metal on the alumina. Table 7.2 shows the color change of the catalyst before and after use. Thermogravimetric analysis under an air stream (Figure 7.3) shows the

Table 7.2 Physical and Chemical Changes of the Promoted Catalysts Before and After Use

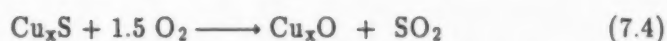
Catalyst	Color		M-S Break Temp. Shown in TGA
	Before use	After use	
Iron-Alumina	Brown (Fe_2O_3)	Black (Fe_xS_y)	> 267°C
Copper- Al_2O_3	Yellow-Green (CuO)	Black (Cu_xS)	—
Zinc-Alumina	White (ZnO)	White (ZnS)	> 479°C
Sodium- Al_2O_3	White (Na_2O)	White (Na_2O)	—

weight loss of these catalysts after use, scanning from 30 to 700°C. Both alumina (Kaiser 201) and sodium-doped alumina showed a weight loss corresponding to water desorption only. But for the transition-metal-doped catalysts, an additional weight loss stage appeared after the water desorption stage. Figure 7.2 shows that before use, all these fresh prepared catalysts did not show this additional weight loss in the TGA curve. From the evidence of the changes of color and TGA curves for the catalysts before and after use, the transition-metal-doped catalysts were most likely sulfided. The TGA picture suggests that the following reactions most likely took place during the thermogravimetric measurements in the air stream.

For Fe- and Zn- doped alumina:



For Cu-doped alumina:



$$x = 1 \text{ or } 2$$



With increasing temperature during the TG analysis, the Cu-alumina catalyst after use exhibited increases in weight between 250°C and 390°C as shown by curve c in Figure 7.3. This suggests that reaction (7.5) may take place during the TG analysis. The Cu-doped catalyst may be partly reduced by H₂S gas. For Fe- or Zn- doped catalyst, the TGA curves do not show weight-gain of the samples with increasing temperature in the air stream because only one reaction, (7.2) or (7.3), may take place during the TG analysis. Reactions (7.2) and (7.3) will result in weight loss only. That the various metal sulfides were oxidized at different temperatures, as shown in TGA Figure 7.3, may be related to their different M-S

Figure 7.2 Thermogravimetric Analysis of the Promoted Catalysts Before Use

- | | |
|------------------------|------------------------|
| a. Zn-Alumina Catalyst | d. Na-Alumina Catalyst |
| b. Fe-Alumina Catalyst | e. Alumina Kaiser 201 |
| c. Cu-Alumina Catalyst | |

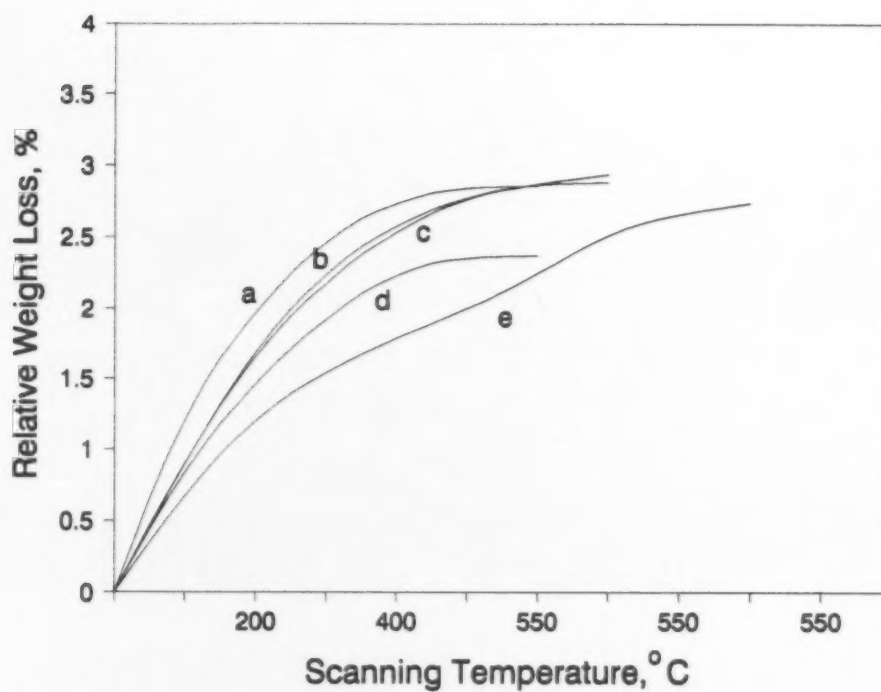
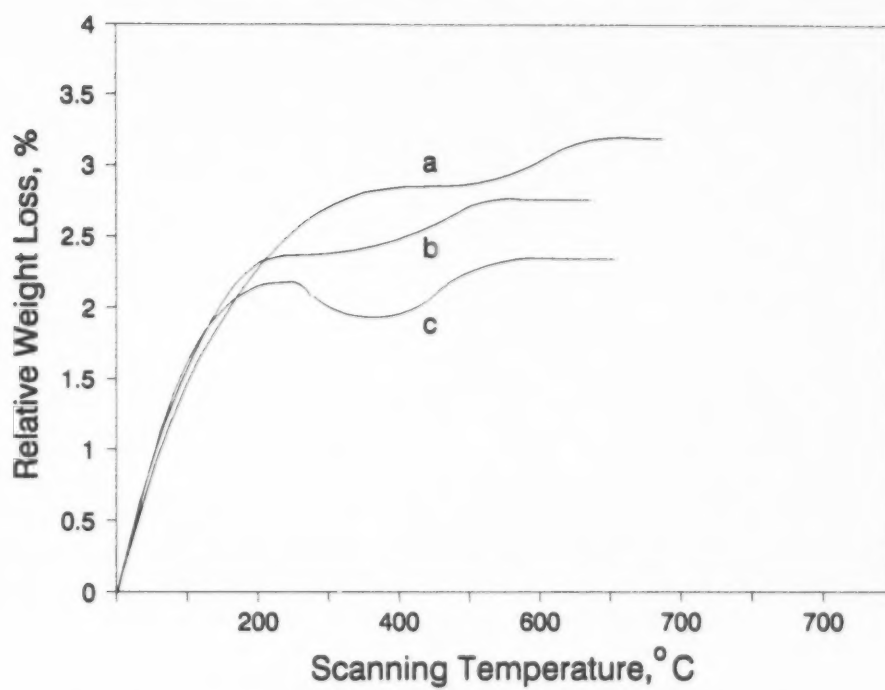


Figure 7.3 Thermogravimetric Analysis of the Promoted Catalysts After Use

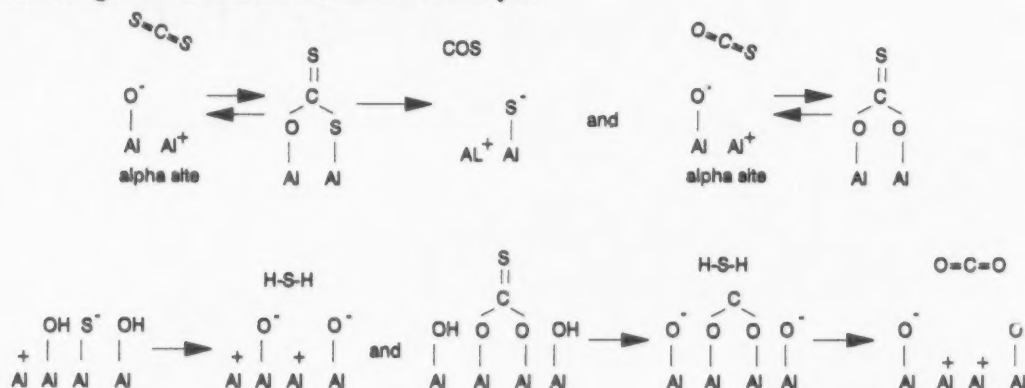
- a. Zn-Alumina Catalyst
- b. Fe-Alumina Catalyst
- c. Cu-Alumina Catalyst



bond strengths.

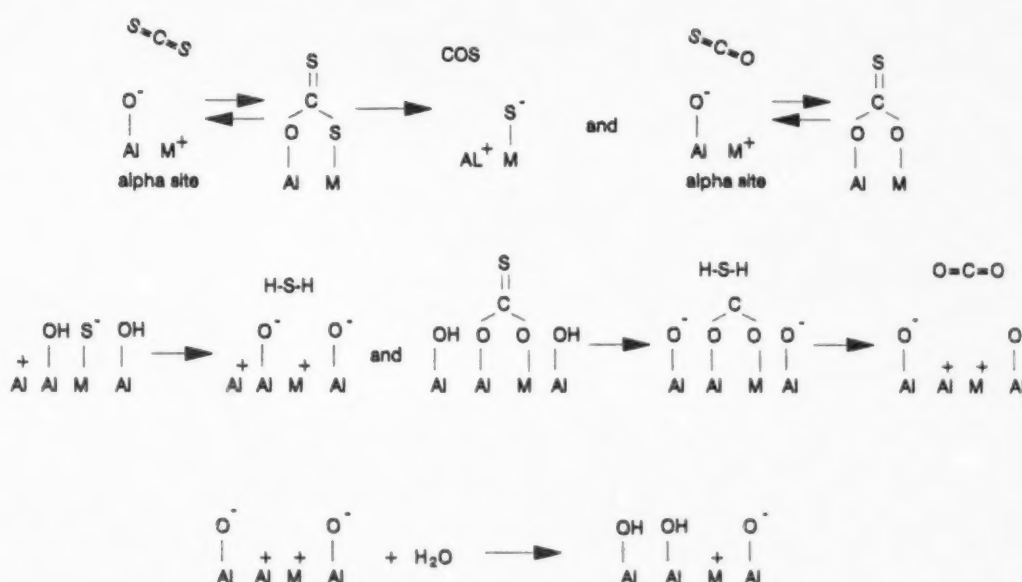
During the CS_2 hydrolysis reaction, H_2S is one of the products. Either the transition metal was slowly sulfided or the surface metal sulfide was in equilibrium with the gas phase H_2S produced by a stoichiometric amount from the CS_2 conversion. When additional H_2S was introduced into the system, the elevated H_2S concentration in the gas phase might accelerate the metal sulfidation speed and increase the surface metal sulfide concentration on the alumina surface. At a higher temperature (340°C), the metal oxide on the alumina surface could be quickly sulfided by H_2S gas solely produced from the CS_2 hydrolysis even though the H_2S concentration in gas phase was low (< 1.0 mol %, depends on the amount of CS_2 converted). So, the introduction of additional H_2S from feed did not change the CS_2 conversion at the high temperature (340°C). It is apparent from the results shown in Figure 7.1 (dotted line) that the sulfidation of the metal increases the catalyst activity for the CS_2 hydrolysis reaction, and the gas-phase H_2S favored the formation of metal sulfide on the catalyst surface.

The hydrolysis of CS_2 involved S/O exchange. Extending the mechanism proposed by Pearson (1992) for CS_2 hydrolysis to COS hydrolysis as well gives the following mechanism on an alumina catalyst:





When the alumina is doped with metals which are sulfided, the adsorption center may shift to the surface metal sulfide as follows:

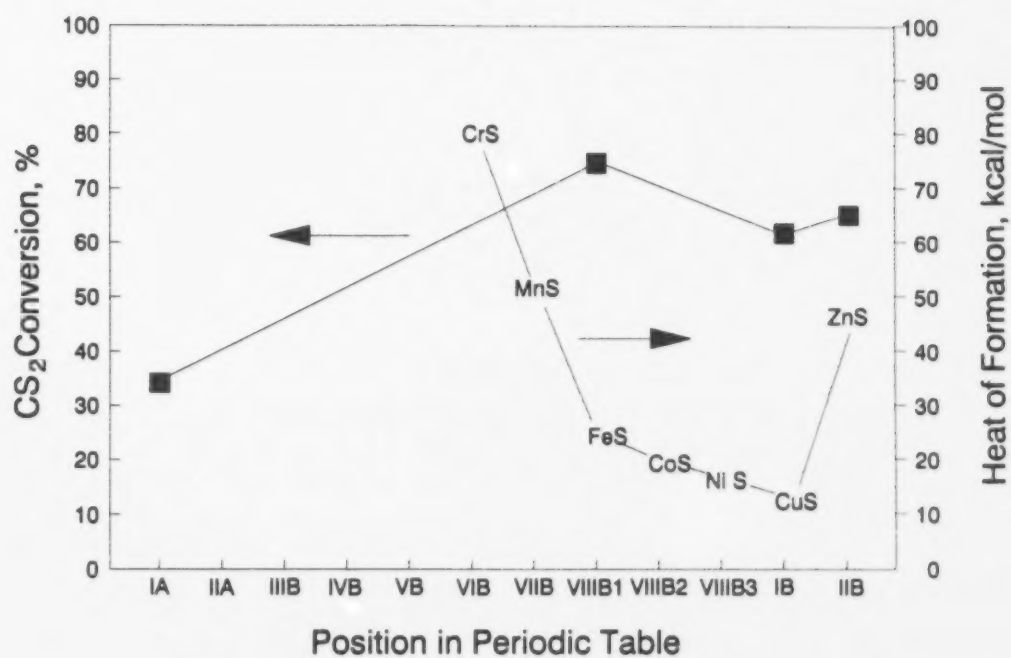


From the consideration of surface geometry factor, the doped metals (Cu^{2+} : ionic radius = 0.072 nm; Fe^{2+} : ionic radius = 0.074 nm; Zn^{2+} : ionic radius = 0.074 nm) (Weast and Astle, 1982) have larger size than Al^{3+} ion (ionic radius: 0.051 nm) on the surface which may result in a more comfortable bonding to S^{2-} ion (ionic radius: 0.184 nm) of CS_2 molecule. Therefore, the opportunity for the adsorption of CS_2 on the surface was likely increased. Furthermore, as the above picture shows, the surface M-S bond may also participate in the CS_2 hydrolysis, acting as a bridge which offers a smaller energy barrier for the S/O exchange during the reaction.

7.3.3 Periodic Trends in the CS₂ Hydrolysis Activity of Promoted Catalysts

Figure 7.4 shows that the activity of the promoted catalysts was related to the position of the transition metal in the periodic table. Of the four promoted catalysts tested at 230°C, the maximum activity occurred on the iron-promoted catalyst. The shape of the curve over the rest of the temperatures tested remained essentially the same. As mentioned above, the S/O exchange occurred during the hydrolysis of CS₂. Therefore, if the M-S bond participated in the S/O exchange, the activity may relate to the strength of the M-S bond. The strength of the bond may be proportional to the heat of formation of the bond. A plot of the catalyst activity with the heat of formation of the M-S compounds (Weast and Astle, 1982) versus its position in the periodic table shows that the change of catalyst activity is related to the heat of formation of the M-S bond. The Cu-S bond, having the smallest heat of formation, possessed the least activity. The Zn-S bond, though having a much greater heat of formation than either Fe-S or Cu-S bond, also had a lower activity. These facts follow the well-known principle of Sabatier (Moffat, 1990) which states that for a catalyst exhibiting maximum activity in a given reaction, the surface complexes formed between the catalyst and the reacting molecule will have intermediate heats of formation. The Fe-S bond appeared to have the most suitable intermediate heat of formation among the catalysts tested. Further analysis of our limited results shown in Figure 7.4 indicated that the transition metals, Co and Ni, were not expected to have higher activity than the iron. The transition metals at the left side of iron have a heat of formation of M-S bond even greater than zinc. So, from Sabatier's principle, these metals are also not expected to be more active than the iron promoted catalyst. The Ti and V are difficult to sulfide and so, their promotion effect, if any, toward CS₂ hydrolysis could not be tested. The second row of transition metals, usually

Figure 7.4 Periodic Trends in the CS₂ Hydrolysis Activity of the Promoted Catalysts



expensive, were not tested in the experiments.

7.4 CONCLUSIONS

1. The iron promoted alumina catalyst showed the highest activity for CS₂ hydrolysis among the catalysts tested. During the reaction, metal sulfides were formed on the transition-metal-doped alumina catalysts. These sulfides were identified as promoters of the CS₂ hydrolysis reaction.
2. The activity of the transition metal for CS₂ hydrolysis appeared to relate to its position in the periodic table. From the correlation of catalyst activity with the heat of the formation of a M-S bond, the iron appeared to be the best promoter for CS₂ hydrolysis among the first row of transition metals on the periodic table.

7.5 NOMENCLATURE

C _o	=	Inlet CS ₂ concentration, mol %
C _e	=	Outlet CS ₂ concentration, mol %

7.6 BIBLIOGRAPHY

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- Moffat, J. B., "Theoretical Aspects of Heterogeneous Catalysis", Chapter 6, p 206–255, 1990, Van Nostrand Reinhold, New York.
- R. C. Weast and M. J. Astle, CRC Handbook of Chemistry and Physics, CRS Press Inc. Boca Raton, Florida, 63rd Edition (1983).

CHAPTER 8

CONCLUSIONS

1. The performance of industrial catalysts used in the modified Claus process must be suitable not only for the $\text{H}_2\text{S}/\text{SO}_2$ reaction to produce elemental sulfur but also for the hydrolysis of COS and CS_2 . The activity of titania- and bauxite-based catalysts appears to be better for the hydrolysis reactions.
2. The activity of the titania-based catalyst (CRS 31 tested) for the hydrolysis of CS_2 , which exhibits more sensitive behavior to the reaction temperature, appears to be related to its less hydrophilic behavior as compared to the alumina-based catalysts. Above 290°C , the titania catalyst is more hydrophobic which may be responsible for its higher activity for the hydrolysis reactions than the alumina catalysts.
3. The measurement of pore size distributions of the alumina- and titania-based catalysts and the prediction of capillary condensation of sulfur in the two types of catalysts (using the Kelvin equation) indicates a major blockage of pore volume for alumina-based catalyst (Kaiser 201) because of its narrow PSD and smaller pore radii whereas the pores of the titania-based catalyst (CRS 31) were not severely affected in the temperature ranges encountered in modified Claus process. A modification of the alumina catalyst with larger pore sizes may be beneficial to sulfur recovery plants, especially for the cold-bed Claus converters.
4. Intrinsic kinetic models were developed for both CS_2 and COS hydrolysis reactions over both titania and alumina catalysts. The applicability of such models in the simulation of simultaneous CS_2 and COS hydrolysis reactions

appears to be deficient and model modification are required.

5. Catalysts used in modified Claus process converters are generally cylindrical extrudates or spheres in their physical form. Increases in external area and lowering of bed pressure drop may be achieved using other shapes. This work suggests that such improvements would be advantageous to sulfur recovery plants.
6. The computer simulation of Claus catalytic converter performances, in which both the $\text{H}_2\text{S}/\text{SO}_2$ and hydrolysis reactions occur simultaneously, is now, in principle, possible. The reliability of such predictions remains to be demonstrated.
7. The computer simulation of the CS_2 and COS hydrolysis reactions which employ the kinetic models developed herein predicts hydrolysis conversions which tend to be low, hence conservative.
8. Iron appears to be a suitable promoter for alumina-based catalysts. Additional experimental verification of the bifunctional role of this promoted catalyst is needed.

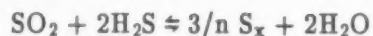
CHAPTER 9

RECOMMENDATION FOR FUTURE WORK

From the results of this research on CS_2 and COS hydrolysis and the model simulations, the following recommendations are offered:

1. The high water concentration in the Claus converter does not favor the hydrophilic alumina catalyst for the hydrolysis of CS_2 and COS . A modification to make the alumina catalyst become less hydrophilic should be further pursued. Adding transition metals (Fe , Cu , etc) which have showed positive function for the hydrolysis of CS_2 may help to reduce hydrophilicity of the alumina surface. The hydrolysis reactions should also be tested at higher water concentrations (15 % – 30 %), which requires experimental equipment operable under high water concentrations.
2. Since the experiments for the hydrolysis of CS_2 and COS were made independently, the kinetics network for the co-hydrolysis of CS_2 and COS suggested in this thesis should be tested further by a feed containing both CS_2 and COS .
3. The rate of catalyst deactivation in the kinetics of CS_2 and COS hydrolysis merits further study using the CS_2 and COS rate functions obtained in this work. Thereby, simulation studies of a Claus converter could become more realistic.
4. Alumina catalyst particles with the geometry of a hollow cylinder or a solid cylinder are suggested to replace the spherical alumina catalyst currently used in sulfur recovery plants. Their higher activity for CS_2 and COS conversions may extend the life-time of the catalyst used in Claus units. In addition, using a hollow cylindrical catalyst may also reduce pressure drop, ΔP , across the adiabatic reactor and thereby save the cost of driving power for the process.

5. Iron-promoted alumina catalyst should be further tested for the simultaneous reactions,



$$n = 3, 6, 8$$

and



to obtain the following information:

- a. the nature of the interactions on the catalyst surface for both the CS_2/COS hydrolysis and Claus reaction.
- b. the stability of FeS on the alumina surface when the feed condition becomes oxidizing, for example, by the introduction of a trace of O_2 into the system.

If positive results are obtained from the experiments cited in a and b, further optimization of the ratio of iron on alumina should be determined on a small laboratory scale apparatus.

APPENDICES

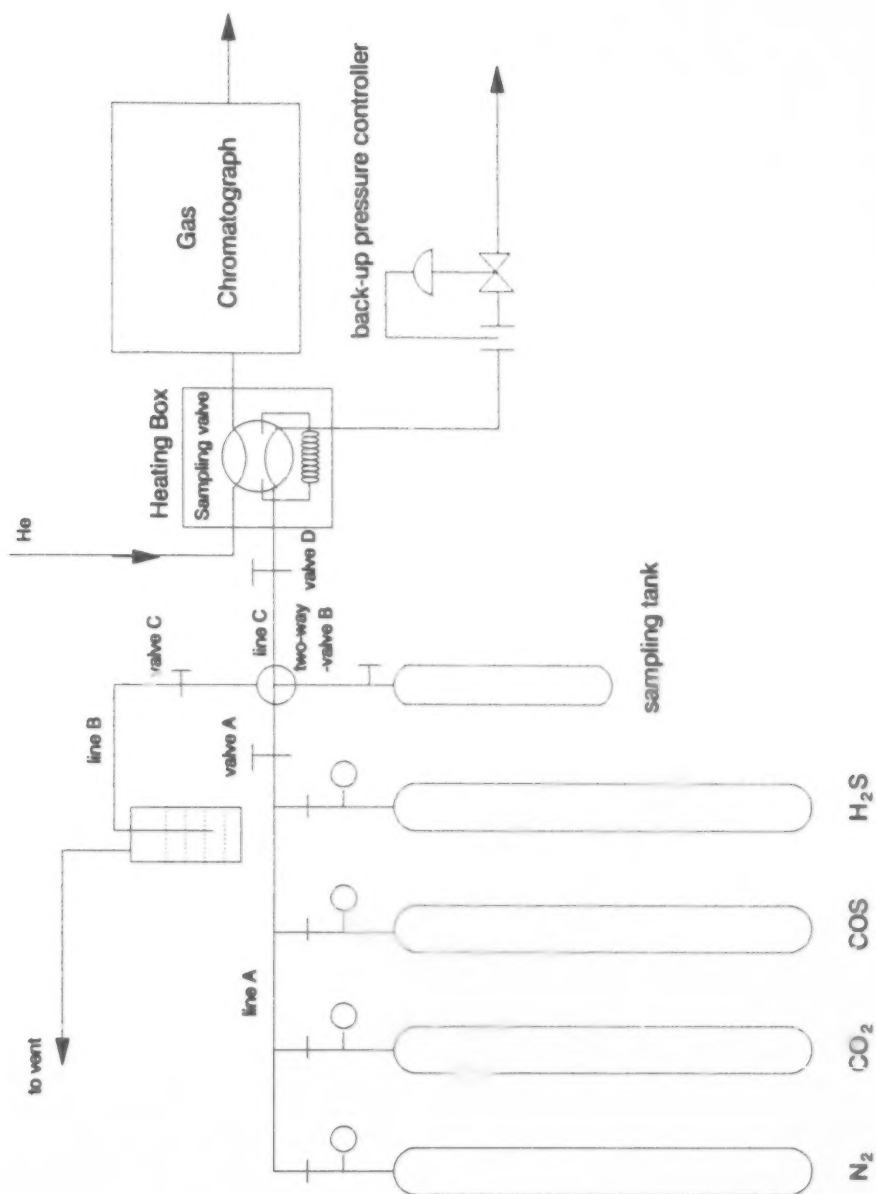
A. CALIBRATION OF EXPERIMENTAL EQUIPMENT

A.1 Calibration of Gas Chromatography

A sketch of the apparatus used for gas chromatographic calibration of CO_2 , COS and H_2S is shown in Figure A-1. To start a calibration for gas sample: CO_2 , COS and H_2S , an accurate sample of calibration gas was made first. Referring to Figure A-1, the procedure for making up calibration mixture is now described step-by-step:

1. Switch the two-way-valve to a position connecting lines A and B. Open valves A, C and the sampling cylinder.
2. Flush lines A and B with pure nitrogen to eliminate all other gases which may be present.
3. Close valve C and fill the sampling cylinder with pure nitrogen until its pressure equilibrates to the supply pressure of the nitrogen tank (60 psig).
4. Close valve A. Open valve C to allow the sampling cylinder to vent until no bubble was seen in the water bottle installed at the end of line B.
5. Repeat operating steps 2 and 3 three times to eliminate other gases in the sampling cylinder.
6. Close valves A and C, take off the sampling cylinder from line and obtain its weight, W_1 , on a balance.
7. Switch the two-way-valve to the position connecting lines A and C and open valve D. Purge lines A and C with the desired calibration gas: CO_2 , COS or H_2S , until the on-line GC analysis shows one peak for the desired calibration gas only.
8. Turn off valve D and open the sampling cylinder to allow it to be

Figure A-1 Apparatus used for gas chromatographic calibration



pressurized by the desired calibration gas to the pre-determined pressure.

Then, obtain weight of the sampling cylinder, W_2 .

9. Repeat steps 6 and 7 with pure nitrogen gas and obtain the total weight of the sampling cylinder, W_t

With above method, a standard calibration gas was prepared. The composition of the calibration gas in the sampling cylinder is calculated as follows:

$$\text{mol \%} = \frac{N_i}{N_i + N_{N_2}} = \frac{(W_2 - W_1)/M_i}{(W_2 - W_1)/M_i + (W_t - W_2)/M_{N_2}} \quad (\text{A-1})$$

where, $i = \text{CO}_2, \text{COS or H}_2\text{S}$.

During the calibration process, the calibration gas with known composition was allowed to flow through the GC sampling valve which was held in a heating box constant at 100°C . The flowing calibration gas pressure was controlled by a Foxboro back pressure controller at 1.5 atm. This condition was maintained during the calibration and for all the experiments afterwards.

The gas chromatograph was operated at the conditions outlined in Chapter 2. For every analysis, the peak areas of the chromatograms were measured by an integrator on the recorder and since about 5 analysis of various sample sizes were obtained, an average area was used and plotted as abscissa. The corresponding compositions (mol %) were plotted as ordinates to obtain the straight lines shown in Figure 3.4 of Chapter 2. A summary of the least squares coefficients for straight line fitting of the data is given in Table A-1.

The calibration of CS_2 and H_2O is detailed in the following section.

Table A-1 Least squares fit of gas chromatography data
for CO₂, COS and H₂S

CO ₂ Area	CO ₂ mol %		PCT Error
Measured	Prepared	Calculated	
33250	6.07	6.05	0.33
26312	4.91	4.79	6.28
15831	2.72	2.88	5.88
3323	0.612	0.60	1.18
250	0.046	0.0455	0.87

Coefficient of the straight line = 0.000197

Rsquare	= 0.998239
Standard deviation	= 0.110918
Standard error of coefficient	= 0.000002

COS Area	COS mol %		PCT Error
Measured	Prepared	Calculated	
203900	17.70	18.15	2.53
99277	9.39	8.83	5.91
70464	6.36	6.27	1.42
21970	1.98	1.96	1.25
5316	0.48	0.47	0.39

Coefficient of the straight line = 0.000089

Rsquare	= 0.989949
Standard deviation	= 0.668647
Standard error of coefficient	= 0.000002

H ₂ S Area	H ₂ S mol %		PCT Error
Measured	Prepared	Calculated	
105900	18.20	17.68	2.82
43958	7.26	7.34	1.07
22704	4.10	3.96	3.47
8205	1.42	1.37	3.50
3324	0.57	0.56	3.12

Coefficient of the straight line = 0.000167

Rsquare	= 0.992884
Standard deviation	= 0.600741
Standard error of coefficient	= 0.000005

A.2 Calibration of Feed System

The feed system involves bubbling an inert carrier gas (N_2) through a H_2O saturator or CS_2 saturator to carry CS_2 and H_2O reactants to the reactor. By maintaining the saturator at different temperatures, various amounts of H_2O or CS_2 could be introduced into the reactor.

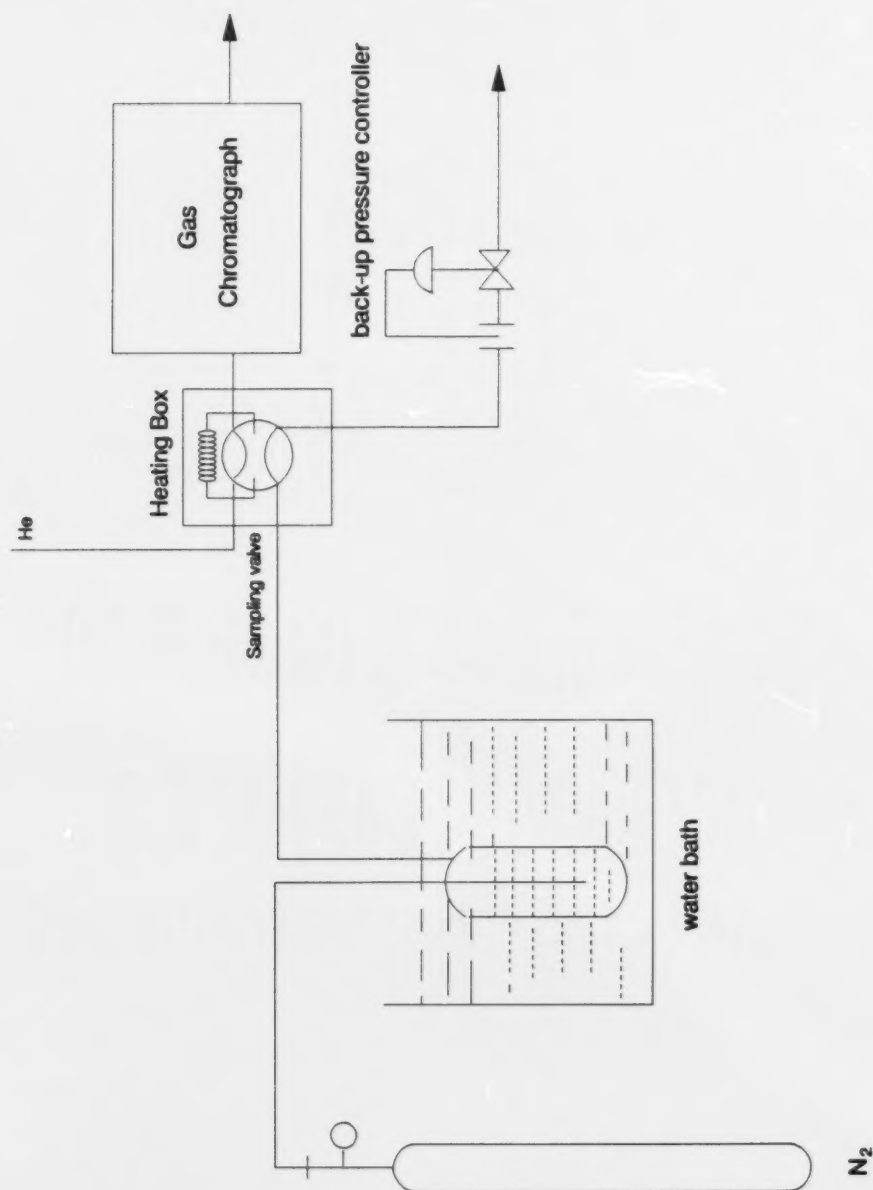
A schematic sketch of the apparatus used for the feed system together with its calibration equipment is shown in Figure A-2. The saturators for H_2O and CS_2 are made of glass with 1000 mL size. A fine-pore filter was installed at the end of the gas bubbling tube as a gas distributor. All lines after the saturator were wound with michrome heating wire to prevent condensation.

The procedure for calibrating H_2O is now described as follows: the H_2O saturator was immersed in a water bath which temperature was controlled by a Thermomix 1420 regulator at a desired temperature. The on-line gas pressure was controlled by a Foxboro back pressure controller at 1.5 atm. A controlled nitrogen stream saturated with H_2O vapor passed the sampling valve which was housed in a heating box at constant temperature of $100^\circ C$ and was then analyzed by the gas chromatograph. This procedure was repeated with two consecutive H_2O saturators to check if the nitrogen stream was saturated with H_2O or not. Since the H_2O peak area did not change with the number of saturators used, the H_2O vapor pressure in gas phase reached equilibrium at the controlled water bath temperature. The corresponding H_2O concentration in the gas line was determined as follows:

$$\text{mol \%} = N_{H_2O}/N_t = P_{H_2O}^0/P_t \quad (A-2)$$

The H_2O vapor pressure at current bath temperature could be calculated by equation (A-3).

$$\ln P_w^0 = 25.696 - 5288.80/T, \text{ Pa} \quad (A-3)$$

Figure A-2 Apparatus used for Calibration of CS₂ hydrolysis feed system

By repeating the above procedures at different bath temperature, various H₂O vapor concentrations were obtained. The corresponding peak areas of the chromatograms were measured by an integrator. For the calibration of CS₂, the water bath was replaced by a refrigerated bath and similar runs were repeated. Equation (A-4) was used for the calculation of CS₂ vapor pressure.

$$\ln P_{\text{CS}_2}^0 = 22.558 - 3521.94/T, \text{ Pa} \quad (\text{A-4})$$

Equations (A-3) and (A-4) were obtained from regression of the data presented in "Handbook of Physics and Chemistry" (63rd edition, D-196 and D-204).

A plot of mol % versus peak area is shown in Figure 3.4 of Chapter 2. A summary of the least square coefficients for straight line fitting of the data is given in Table A-2.

Table A-2 Least squares fit of gas chromatograph Data for H₂O and CS₂

H ₂ O Area	H ₂ O, mol %		PCT Error
Measured	Prepared	Calculated	%
18845	3.19	3.17	0.63
10653	1.75	1.79	2.29
5718	1.00	0.96	3.65
3474	0.61	0.58	3.53
2451	0.42	0.41	1.96

Coefficient of the straight line = 0.000168

Rsquare	= 0.999250
Standard deviation	= 0.030777
Standard error of coefficient	= 0.000001

CS ₂ Area	CS ₂ mol %		PCT Error
Measured	Prepared	Calculated	%
120960	5.00	4.96	0.81
69700	2900	2.86	1.45
43386	1.84	1.78	3.33
27278	1.16	1.12	3.59
13250	0.53	0.54	2.50

Coefficient of the straight line = 0.000041

Rsquare	= 0.999011
Standard deviation	= 0.055414
Standard error of coefficient	= 0.000001

A.3 Calibration of Mass Flow Meter

The experiments used three mass flow meters to provide feed gas flow. Mass flow meters MFM₁ and MFM₃ maintained N₂ feed flow and MFM₂ provided H₂S or CO₂ gas to feed. To calibrate the three mass flow meters for each specific gas, a calibration apparatus was constructed and a schematic sketch is shown in Figure A-3. A soap bubble meter or a precision wet-test meter was used to measure the gas flow rate depending on the ranges of gas flow rate to be calibrated. For each specific gas, flow rates were measured against percentage setting of the mass flow meter at 25, 50, 75 and 100. For each point, an average five consecutive flowrate measurements was taken as the ordinate. The corresponding mass flow meter percentage settings were plotted as the abscissae to obtain the straight lines shown in Figure A-4.

Figure A-3 Apparatus used for calibration of Mass flow meter

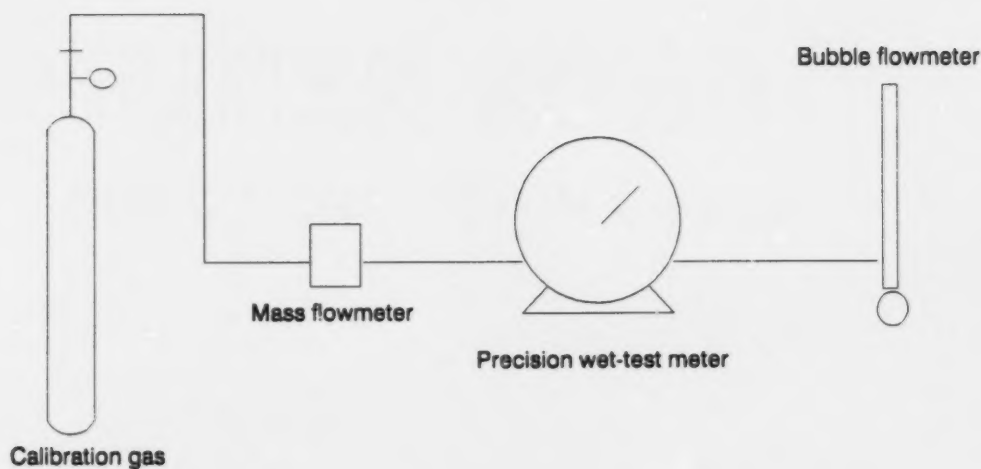
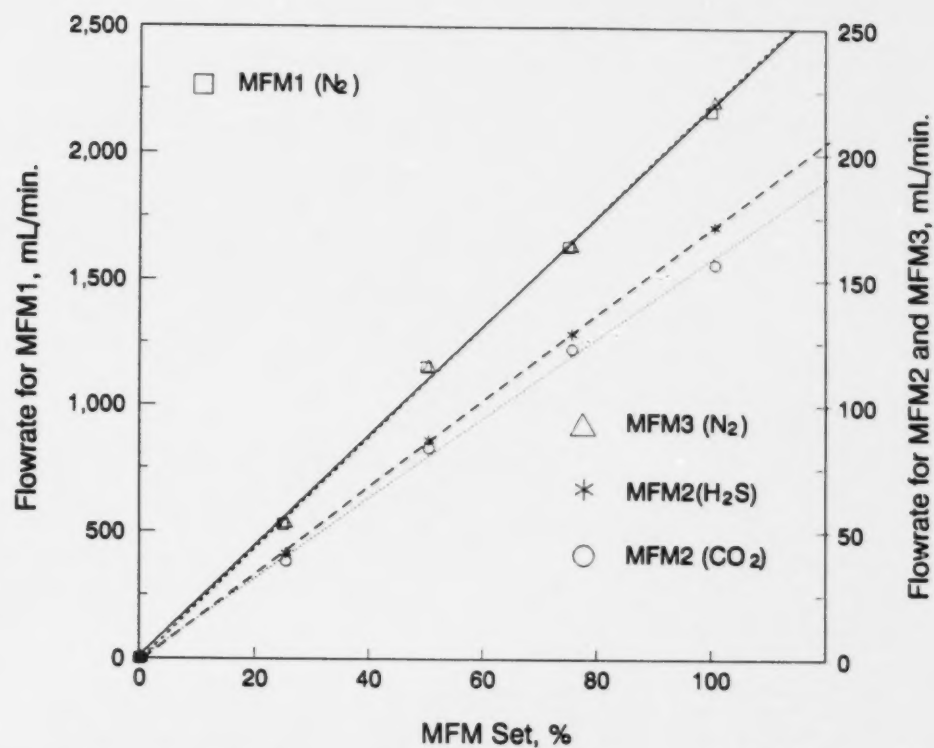


Figure A-4 Mass flow meter calibration lines



A summary of the least squares coefficients for straight line fitting of the data is given in Table A-3 to A-6.

Table A-3 Least squares of calibration data for mass flow meter MFM₁ at 22°C and atmospheric pressure

MFM Set %	Calibration gas, N ₂		Error (%)
	Observed (mL/min)	Calculated (mL/min)	
0	0	0	—
25	527.8	546.8	0.45
50	1150.4	1093.6	4.94
75	1632.8	1640.4	0.47
100	2169.3	2187.2	0.83

Coefficient of the straight line = 21.87226

Rsquare = 0.99866

Standard deviation = 31.48574

Table A-4 Least squares of calibration data for mass flow meter MFM₃
at 22°C and atmospheric pressure

MFM Set %	Calibration gas, N ₂		Error (%)
	Observed (mL/min)	Calculated (mL/min)	
0	0	0	—
25	53.3	55.2	3.56
50	115.2	110.4	4.17
75	163.4	165.6	1.34
100	220.5	220.8	0.13

Coefficient of the straight line = 2.207866

Rsquare = 0.99896

Standard deviation = 2.809789

Table A-5 Least squares of calibration data for mass flow meter MFM₂
at 22°C and atmospheric pressure

MFM Set %	Calibration gas, CO ₂		Error (%)
	Observed (mL/min)	Calculated (mL/min)	
0	0	0	—
25	38.6	40.0	3.56
50	83.2	79.9	3.91
75	122.6	119.9	2.19
100	156.6	159.9	2.10

Coefficient of the straight line = 1.598933

Rsquare = 0.99807

Standard deviation = 2.761279

Table A-5 Least squares of calibration data for mass flow meter MFM₂
at 22°C and atmospheric pressure

MFM Set %	Calibration gas, H ₂ S		Error (%)
	Observed (mL/min)	Calculated (mL/min)	
0	0	0	—
25	41.7	42.9	2.87
50	86.5	85.8	0.82
75	134.2	128.7	4.11
100	167.4	171.6	2.50

Coefficient of the straight line = 1.715866

Rsquare = 0.99728

Standard deviation = 3.529152

B. REDUCTION OF DATA AND ERROR ANALYSIS

A step by step procedure is outlined below which indicates how a set of experimental measurements is reduced to kinetic data and a print out using Minitab package for the calculation of the sample data set is listed afterwards. The sample calculation is given for run number DC-21 for which the following measurements were taken:

Reactor temperature:	300°C
Reactor Wall Temperature:	302°C
Reactor pressure	150 kPa
Feed flow rate	0.03 m ³ /h
Catalyst weight	2.01 g

	Chromatogram Results						
	Feed		Product				
	CS ₂	H ₂ O	CS ₂	H ₂ O	H ₂ S	CO ₂	COS
Area	12915	11538	8291	9717	1704	748	359
Area	13098	11785	8180	9852	1670	744	360
Area	12786	11807	8445	10036	1812	781	369
Area	13042	11531	8351	9910	1721	753	373
Area5	12801	11856	8254	10068	1743	781	360
Average	12928	11703	8302	9917	1730	761	364

In the following, a sample calculation is described step-by-step. A print out from the results obtained by running the Minitab package using the same

example data is listed in Table B-1 afterwards.

Feed:

$$\text{CS}_2 \text{ mol } \% = 0.000410 \times 12928 = 0.530$$

$$\text{H}_2\text{O mol } \% = 0.000168 \times 11726 = 1.970$$

$$P_{\text{CS}_2} = \text{CS}_2 \text{ mol } \% \times P_t = 0.53 \% \times 150 = 0.795 \text{ kPa}$$

$$P_{\text{H}_2\text{O}} = \text{H}_2\text{O mol } \% \times P_t = 1.97 \% \times 150 = 2.955 \text{ kPa}$$

Product:

$$\text{CS}_2 \text{ mol } \% = 0.000041 \times 8304 = 0.340$$

$$\text{H}_2\text{O mol } \% = 0.000168 \times 9917 = 1.666$$

$$\text{CO}_2 \text{ mol } \% = 0.000197 \times 761 = 0.150$$

$$\text{H}_2\text{S mol } \% = 0.000167 \times 1730 = 0.289$$

$$\text{COS mol } \% = 0.000089 \times 364 = 0.032$$

$$P_{\text{CS}_2} = \text{CS}_2 \text{ mol } \% \times P_t = 0.340 \% \times 150 = 0.510 \text{ kPa}$$

$$P_{\text{H}_2\text{O}} = \text{H}_2\text{O mol } \% \times P_t = 1.666 \% \times 150 = 2.505 \text{ kPa}$$

$$P_{\text{CO}_2} = \text{CO}_2 \text{ mol } \% \times P_t = 0.150 \% \times 150 = 0.225 \text{ kPa}$$

$$P_{\text{H}_2\text{S}} = \text{H}_2\text{S mol } \% \times P_t = 0.289 \% \times 150 = 0.435 \text{ kPa}$$

$$P_{\text{COS}} = \text{COS mol } \% \times P_t = 0.032 \% \times 150 = 0.0480 \text{ kPa}$$

Conversion of CS_2 :

$$\begin{aligned} \text{conv. } \% &= \frac{(\text{CS}_2 \text{ mol } \%)_{\text{feed}} - (\text{CS}_2 \text{ mol } \%)_{\text{product}}}{(\text{CS}_2 \text{ mol } \%)_{\text{feed}}} \times 100 \\ &= (0.530 - 0.340)/0.530 = 35.85 \end{aligned}$$

Reaction rate of CS₂:

Correction of Feed flow rate to reaction temperature and pressure

$$F_t = 0.03 \times \frac{273+300}{273} \times \frac{1}{1.5} = 0.0420 \text{ m}^3/\text{h}$$

$$\begin{aligned} -r_{\text{CS}_2} &= \frac{\{(P_{\text{CS}_2})_{\text{feed}} - (P_{\text{CS}_2})_{\text{prod}}\} F_t}{W R T} = \\ &= \frac{(0.795 - 0.510) \times 0.0420}{0.00201 \times 8.314 \times 573} = 0.00126 \text{ mol/h/g} \end{aligned}$$

Table B-1 Example results using Minitab package

MTB > # Read peak area from data disk in drive a:

MTB > EXECUTE 'A:DATA1'

MTB > #PRINT PEAK AREA

MTB > PRINT C1-C7

ROW	CS2in	H2Oin	CS2out	H2Oout	CO2out	H2Sout	COSout
1	12915	11538	8291	9717	1704	748	359
2	13098	11785	8180	9852	1670	744	360
3	12786	11807	8445	10036	1812	781	369
4	13042	11531	8351	9910	1721	753	373
5	12801	11856	8254	10068	1743	781	360

MTB > LET C11=0.000041*C1

MTB > LET C12=0.000168*C2

MTB > LET C13=0.000041*C3

MTB > LET C14=0.000168*C4

MTB > LET C15=0.000167*C5

MTB > LET C16=0.000197*C6

MTB > LET C17=0.000089*C7

MTB > #PRINT mol %

MTB > PRINT C11-C17

ROW	CS2in	H2Oin	CS2out	H2Oout	CO2out	H2Sout	COSout
1	0.52952	1.93838	0.33993	1.63239	0.28464	0.14743	0.03191
2	0.53700	1.97988	0.33538	1.65521	0.27895	0.14648	0.03200
3	0.52424	1.98358	0.34624	1.68601	0.30261	0.15381	0.03281
4	0.53470	1.93721	0.34239	1.66493	0.28741	0.14830	0.03319
5	0.52485	1.99181	0.33841	1.69135	0.29115	0.15382	0.03201

MTB > LET C21=C11*150/100
 MTB > LET C22=C12*150/100
 MTB > LET C23=C13*150/100
 MTB > LET C24=C14*150/100
 MTB > LET C25=C15*150/100
 MTB > LET C26=C16*150/100
 MTB > LET C27=C17*150/100

MTB > #PRINT PARTIAL PRESSURE
 MTB > PRINT C21-C27

ROW	CS2in	H2Oin	CS2out	H2Oout	CO2out	H2Sout	COSout
1	0.79429	2.90758	0.50989	2.44858	0.42696	0.22114	0.047867
2	0.80550	2.96982	0.50307	2.48282	0.41843	0.21972	0.048005
3	0.78636	2.97536	0.51936	2.52901	0.45392	0.23071	0.049227
4	0.80205	2.90581	0.51358	2.49740	0.43112	0.22246	0.049789
5	0.78728	2.98771	0.50762	2.53702	0.43672	0.23073	0.048023

MTB > LET C31=(C1-C3)/C1
 MTB > LET C31=(C11-C13)/C11
 MTB > LET K1=0.03*(273+300)/273/1.5
 MTB > LET C32=(C21-C23)*K1/8.314/573/0.002

MTB > #PRINT CONVERSION AND RATE
 MTB > PRINT C31 C32

ROW	CS2conv	CS2rate
1	0.358049	0.0012530
2	0.375457	0.0013325
3	0.339531	0.0011763
4	0.359658	0.0012709
5	0.355228	0.0012322

MTB > #PRINT MEAN VALUE AND ERROR ANALYSIS RESULTS

MTB > DESCRIBE C31 C32

	N	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN
CS2conv	5	0.35758	0.35805	0.35758	0.01280	0.00572
CS2rate	5	0.00125	0.00125	0.00125	0.00006	0.00003
		MIN	MAX	Q1	Q3	
CS2conv		0.33953	0.37546	0.34738	0.36756	
CS2rate		0.00118	0.00133	0.00120	0.00130	

Other data obtained by same method of calculation are summarized in Table B-2 to B-7.

Table B-2 Kinetic Data for COS Hydrolysis Over Alumina (Kaiser 201)

Run NO.	Reaction T (°C)	P _t	Inlet P _{COS} (kPa)	P _{H₂O}	Outlet P _{COS} (kPa)	P _{H₂O}	Conv. COS (%)	Rate -r _{COS} (mol/h/g)
DA-1	270	150	0.75	3.0	0.292	2.505	61.07	0.00283
DA-2				6.0	0.349	5.516	53.47	0.00248
BA-3				9.0	0.288	8.315	61.60	0.00286
DA-4				18.0	0.287	17.688	61.73	0.00286
DA-5	270	150	1.5	3.0	0.677	2.078	54.87	0.00508
DA-6				6.0	0.608	5.120	59.47	0.00551
DA-7				9.0	0.666	7.632	55.60	0.00515
DA-8				18.0	0.663	17.223	55.80	0.00517
DA-9	270	150	2.3	3.0	0.947	1.683	58.83	0.00805
DA-10				6.0	0.988	4.709	57.04	0.00780
DA-11				9.0	0.924	7.345	59.83	0.00919
DA-12				18.0	0.920	16.849	60.00	0.00822
DA-13	270	150	2.6	3.0	1.174	1.426	54.85	0.00896
DA-14				6.0	1.088	4.456	58.15	0.00949
DA-15				9.0	1.143	7.003	56.04	0.00916
DA-16				18.0	1.078	16.442	58.54	0.00955
DA-17	270	150	3.0	3.0	1.284	1.203	57.20	0.01060
DA-18				6.0	1.309	4.329	56.37	0.01045
DA-19				9.0	1.242	6.651	58.60	0.01086
DA-20				18.0	1.297	16.477	56.77	0.01052
DA-21	300	150	0.75	3.0	0.242	2.505	67.73	0.00314
DA-22				6.0	0.294	5.516	60.80	0.00282
DA-23				9.0	0.231	8.315	69.20	0.00321
DA-24				18.0	0.229	17.688	69.47	0.00322
DA-25	300	150	1.5	3.0	0.582	2.078	61.20	0.00567
DA-26				6.0	0.499	5.120	66.73	0.00618
DA-27				9.0	0.493	7.632	67.13	0.00622
DA-28				18.0	0.487	17.223	67.53	0.00626
DA-29	300	150	2.3	3.0	0.814	1.683	64.61	0.00887
DA-30				6.0	0.826	4.709	64.09	0.00880
DA-31				9.0	0.815	7.345	64.57	0.00886
DA-32				18.0	0.806	16.849	64.96	0.00892
DA-33	300	150	2.6	3.0	1.028	1.426	60.46	0.00987
DA-34				6.0	0.900	4.456	65.38	0.01065
DA-34				9.0	0.887	7.003	65.88	0.01074
DA-35				18.0	0.876	16.442	66.31	0.01081
DA-36	300	150	3.0	3.0	1.130	1.203	56.67	0.01155
DA-37				6.0	1.096	4.329	63.47	0.01177
DA-38				9.0	1.079	6.651	64.03	0.01187
DA-39				18.0	1.065	16.477	64.50	0.01195
DA-40	330	150	0.75	3.0	0.237	1.994	68.40	0.00362
DA-41				6.0	0.199	5.016	73.47	0.00341
DA-42				9.0	0.253	8.205	66.27	0.00307
DA-43				18.0	0.406	17.167	45.86	0.00213

Table B-2 (Continue)

Run NO.	Reaction T	P _t	Inlet		Outlet		Conv. COS	Rate -r _{cos}
			P _{cos}	P _{H₂O}	P _{cos}	P _{H₂O}		
	(°C)		(kPa)		(kPa)		(%)	(mol/h/g)
DA-44	330	150	1.5	3.0	0.478	1.771	68.13	0.00631
DA-45				6.0	0.491	4.812	67.27	0.00624
DA-46				9.0	0.418	7.790	72.13	0.00669
DA-47				18.0	0.475	16.953	68.33	0.00671
DA-48	330	150	2.3	3.0	0.826	1.490	64.09	0.00880
DA-49				6.0	0.667	4.530	71.00	0.00978
DA50				9.0	0.704	7.582	69.39	0.00955
DA-51				18.0	0.624	16.578	72.87	0.01004
DA-52	330	150	2.6	3.0	0.925	1.259	64.42	0.01050
DA-53				6.0	0.847	4.287	67.42	0.01099
DA-54				9.0	0.757	7.348	70.88	0.01154
DA-55				18.0	0.794	16.338	69.46	0.01131
DA-56	330	150	3.0	3.0	1.159	1.093	61.37	0.01137
DA-57				6.0	0.909	4.059	69.70	0.01292
DA-58				9.0	0.932	7.113	68.93	0.01278
DA-59				18.0	0.843	16.271	71.90	0.01333

Table B-3 Kinetic Data for COS Hydrolysis Over Titania (CRS 31)

Run NO.	Reaction		Inlet		Outlet		Conv. COS (%)	Rate $-r_{\text{COS}}$ (mol/h/g)
	T (°C)	P _t (kPa)	P _{COS} (kPa)	P _{H₂O} (kPa)	P _{COS} (kPa)	P _{H₂O} (kPa)		
DB-1	270	150	0.75	3.0	0.359	2.640	52.13	0.00241
DB-2				6.0	0.309	5.508	58.80	0.00272
DB-3				9.0	0.353	8.660	52.93	0.00246
DB-4				8.0	0.306	17.883	59.20	0.00274
DB-5	270	150	1.5	3.0	0.633	2.071	57.80	0.00536
DB-6				6.0	0.664	5.135	55.73	0.00516
DB-7				9.0	0.615	8.232	59.00	0.00546
DB-8				18.0	0.657	17.223	55.33	0.00521
DB-9	270	150	2.3	3.0	1.032	1.668	55.13	0.00752
DB-10				6.0	0.975	4.709	57.61	0.00788
DB-11				9.0	0.999	7.795	56.57	0.00773
DB-12				18.0	0.933	16.805	59.43	0.00813
DB-13	270	150	2.6	3.0	1.145	1.531	55.96	0.00914
DB-14				6.0	1.168	4.426	55.08	0.00900
DB-15				9.0	1.101	7.453	57.65	0.00942
DB-16				18.0	1.154	16.891	55.62	0.00909
DB-17	300	150	3.0	3.0	1.382	1.338	53.93	0.00999
DB-18				6.0	1.272	4.209	57.60	0.01067
DB-19				9.0	1.322	7.251	55.93	0.01036
DB-20				18.0	1.270	16.470	57.67	0.01069
DB-21	300	150	0.75	3.0	0.299	2.495	60.13	0.00278
DB-22				6.0	0.203	5.298	72.93	0.00338
DB-23				9.0	0.281	7.986	62.53	0.00290
DB-24				18.0	0.212	17.127	71.73	0.00332
DB-25	300	150	1.5	3.0	0.495	1.903	67.00	0.00621
DB-26				6.0	0.537	4.922	64.20	0.00595
DB-27				9.0	0.464	7.429	69.07	0.00640
DB-28				18.0	0.523	16.976	65.13	0.00603
DB-29	300	150	2.3	3.0	0.856	1.563	62.78	0.00861
DB-30				6.0	0.727	4.500	68.39	0.00941
DB-31				9.0	0.780	7.147	66.09	0.00908
DB-32				18.0	0.703	16.732	69.43	0.00956
DB-33	300	150	2.6	3.0	0.926	1.429	64.38	0.01049
DB-34				6.0	0.937	4.284	63.96	0.01043
DB-35				9.0	0.839	7.160	67.73	0.01103
DB-36				18.0	0.892	15.154	65.69	0.01071
DB-37	300	150	3.0	3.0	1.176	1.183	60.80	0.01127
DB-38				6.0	0.971	4.110	67.63	0.01254
DB-39				9.0	1.031	6.806	65.63	0.01217
DB-40				18.0	0.948	15.987	68.40	0.01267
DB-41	330	150	1.5	3.0	0.243	1.994	83.80	0.00777
DB-42				6.0	0.163	5.016	89.13	0.00826
DB-43				9.0	0.220	8.205	85.33	0.00791
DB-44				18.0	0.335	16.868	77.67	0.00720

Table B-3 (Continued)

Run NO.	Reaction Temp P_t		Inlet		Outlet		Conv. COS	Rate $-r_{\text{cos}}$
	(°C)		P_{cos} (kPa)	$P_{\text{H}_2\text{O}}$	P_{cos} (kPa)	$P_{\text{H}_2\text{O}}$	(%)	(mol/h/g)
DB-45	300	150	1.9	3.0	0.424	4.662	77.68	0.00896
DB-46				6.0	0.415	1.771	78.16	0.00902
DB-47				9.0	0.347	7.640	81.74	0.00944
DB-48				18.0	0.488	16.503	74.32	0.00857
DB-49	300	150	2.3	3.0	0.743	1.475	67.70	0.00931
DB-50				6.0	0.564	4.530	75.48	0.01041
DB-51				9.0	0.600	7.358	73.91	0.01019
DB-52				18.0	0.517	6.578	77.52	0.01071
DB-53	300	150	2.6	3.0	0.832	1.259	68.00	0.01108
DB-54				6.0	0.732	4.137	71.85	0.01170
DB-55				9.0	0.637	7.048	75.50	0.01228
DB-56				18.0	0.671	16.188	74.19	0.01207
DB-57	300	150	3.0	3.0	1.066	0.943	64.47	0.01195
DB-58				6.0	0.775	3.759	74.17	0.01375
DB-59				9.0	0.794	6.813	73.53	0.01363
DB-60				18.0	0.700	15.820	76.67	0.01421

Table B-4 Kinetic Data for CS₂ Hydrolysis Over Alumina (Kaiser 201)

Run NO.	Reaction T (°C)	P _t	Inlet P _{CS₂} (kPa)	P _{H₂O}	P _{CS₂}	Outlet P _{H₂O} (kPa)	P _{CO₂}	Conv. CS ₂ (%)	Rate -r _{CS₂} (mol/h/g)
DC-1	270	150	0.795	2.955	0.543	2.501	0.052	31.70	0.00111
DC-2			1.230	2.955	0.853	2.277	0.090	30.65	0.00231
DC-3			1.620	2.955	1.124	2.063	0.118	30.62	0.00304
DC-4			1.965	2.955	1.348	1.844	0.139	31.40	0.00379
DC-5			2.200	2.955	1.576	1.796	0.160	28.36	0.00396
DC-6	270	150	0.930	6.525	0.624	5.956	0.063	32.90	0.00188
DC-7			1.200	6.525	0.825	5.827	0.092	31.25	0.00230
DC-8			1.545	6.525	1.055	5.614	0.108	31.72	0.00301
DC-9			2.565	6.525	1.782	5.068	0.180	30.53	0.00481
DC-10			3.300	6.525	2.299	4.663	0.224	30.33	0.00615
DC-11	270	150	1.545	12.150	1.036	11.323	0.110	32.94	0.00312
DC-12			1.800	12.150	1.221	11.188	0.118	32.17	0.00356
DC-13			2.295	12.150	1.566	10.900	0.175	31.76	0.00448
DC-14			2.715	12.150	1.870	10.677	0.191	31.12	0.00519
DC-15			3.300	12.150	2.288	10.358	0.228	30.67	0.00621
DC-16	270	150	1.545	18.150	1.066	17.202	0.108	31.00	0.00294
DC-17			1.800	18.150	1.244	17.050	0.123	30.89	0.00341
DC-18			2.295	18.150	1.586	16.746	0.162	30.89	0.00435
DC-19			2.715	18.150	1.874	16.485	0.191	30.98	0.00516
DC-20			3.300	18.150	2.290	16.150	0.226	30.61	0.00620
DC-21	300	150	0.795	2.955	0.514	2.505	0.048	35.35	0.00125
DC-22			1.230	2.955	0.813	2.287	0.072	33.90	0.00256
DC-23			1.620	2.955	1.071	2.076	0.101	33.89	0.00337
DC-24			1.965	2.955	1.329	1.937	0.119	32.37	0.00391
DC-25			2.220	2.955	1.546	1.877	0.134	30.36	0.00414
DC-26	300	150	0.930	6.525	0.591	6.963	0.054	36.45	0.00208
DC-27			1.200	6.525	0.791	5.837	0.073	34.04	0.00354
DC-28			2.565	6.525	1.697	5.084	0.180	33.84	0.00533
DC-29			3.300	6.525	2.189	4.681	0.201	33.67	0.00682
DC-30	300	150	1.200	12.30	0.834	11.555	0.074	30.50	0.00409
DC-31			2.288	12.30	1.469	10.878	0.140	35.80	0.00507
DC-32			2.715	12.30	1.764	10.664	0.189	35.03	0.00584
DC-33			3.300	12.30	2.205	10.417	0.203	33.18	0.00672
DC-34	300	150	2.715	18.15	1.748	16.411	0.168	35.62	0.00594
DC-35			1.545	18.15	0.971	17.117	0.91	37.15	0.00353
DC-36			1.800	18.15	1.143	16.969	0.110	36.50	0.00403
DC-37			3.300	18.15	2.184	16.144	0.201	33.82	0.00685
DC-38	330	150	0.795	2.955	0.491	2.518	0.041	38.24	0.00178
DC-39			1.230	2.955	0.776	2.302	0.061	36.91	0.00401
DC-40			1.620	2.955	1.022	2.093	0.080	36.91	0.00529
DC-41			1.965	2.955	1.255	1.835	0.104	36.13	0.00688
DC-42			2.220	2.955	1.442	1.835	0.120	35.05	0.00688
DC-43	330	150	0.930	6.525	0.561	5.989	0.048	39.68	0.00335

Table B-4 (Continue)

Run NO.	Reaction		Inlet			Outlet		Conv. CS ₂ (%)	Rate -r _{CS₂} (mol/h/g)
	T (°C)	P _t	P _{CS₂} (kPa)	P _{H₂O}	P _{CS₂}	P _{H₂O} (kPa)	P _{CS₂}		
DC-44			1.200	6.525	0.727	5.825	0.063	39.42	0.00430
DC-45			1.545	6.525	0.941	5.631	0.083	39.09	0.00549
DC-46			2.565	6.525	1.571	5.054	0.140	38.75	0.00903
DC-47			3.300	6.525	2.016	4.625	0.171	38.91	0.01166
DC-48	330	150	1.545	12.30	0.909	11.333	0.083	41.17	0.00593
DC-49			1.800	12.30	1.077	11.201	0.101	40.17	0.00674
DC-50			2.295	12.30	1.357	10.873	0.122	40.87	0.00876
DC-51			2.715	12.30	1.622	10.638	0.150	40.26	0.01020
DC-52			3.300	12.30	1.961	10.264	0.180	40.58	0.01250
DC-53	330	150	1.545	18.25	0.915	17.167	0.084	40.78	0.00604
DC-54			1.800	18.25	1.072	17.014	0.095	40.44	0.00698
DC-55			2.295	18.25	1.355	16.684	0.123	40.96	0.00900
DC-56			2.715	18.25	1.603	16.416	0.152	40.96	0.01065
DC-57			3.300	18.25	1.957	16.054	0.184	40.70	0.01287

Table B-5 Kinetic Data for CS₂ Hydrolysis Over Titania (CRS 31)

Run NO.	Reaction T (°C)	P _t	Inlet P _{CS₂} (kPa)	P _{H₂O}	P _{CS₂}	Outlet P _{H₂O} (kPa)	P _{CO₂}	Conv. CS ₂ (%)	Rate -r _{CS₂} (mol/h/g)
DD-1	270	150	0.870	2.96	0.577	2.397	0.035	33.68	0.00180
DD-2			1.140	2.96	0.776	2.261	0.044	31.93	0.00224
DD-3			1.365	2.96	0.927	2.121	0.058	32.09	0.00269
DD-4			1.755	2.96	1.176	1.522	0.074	32.99	0.00356
DD-5			2.115	2.96	1.423	1.636	0.091	32.72	0.00425
DD-6	270	150	0.705	3.96	0.459	3.489	0.028	34.89	0.00151
DD-7			1.575	3.96	1.048	2.952	0.068	33.46	0.00324
DD-8			1.935	3.96	1.274	2.696	0.086	34.16	0.00406
DD-9			2.340	3.96	1.550	2.450	0.099	33.76	0.00485
DD-10			2.595	3.96	1.736	2.318	0.112	33.10	0.00527
DD-11	270	150	0.881	11.01	0.578	10.431	0.035	34.39	0.00186
DD-12			1.754	11.01	1.132	9.818	0.078	35.46	0.00382
DD-14			2.355	11.01	1.518	9.405	0.110	35.54	0.00514
DD-15			2.928	11.01	1.928	9.095	0.122	34.15	0.00614
DD-16			3.495	11.01	2.299	8.719	0.138	34.22	0.00734
DD-17	270	150	1.545	18.15	1.035	17.171	0.068	33.01	0.00313
DD-18			1.800	18.15	1.177	16.953	0.080	34.61	0.00383
DD-19			2.295	18.15	1.490	16.605	0.102	35.08	0.00494
DD-20			2.715	18.15	1.761	16.318	0.113	35.14	0.00586
DD-21			3.300	18.15	2.152	15.945	0.130	34.79	0.00705
DD-22	300	150	0.870	2.96	0.482	2.293	0.030	44.60	0.00239
DD-23			1.140	2.96	0.645	2.112	0.040	43.42	0.00304
DD-24			1.365	2.96	0.807	2.004	0.045	40.88	0.00343
DD-25			1.755	2.96	1.019	1.702	0.062	41.94	0.00452
DD-26			2.115	2.96	1.248	1.477	0.075	40.99	0.00532
DD-27	300	150	0.705	3.96	0.400	3.447	0.021	43.26	0.00184
DD-28			1.575	3.96	0.880	2.778	0.055	44.13	0.00425
DD-29			1.935	3.96	1.274	2.696	0.064	34.16	0.00406
DD-30			2.340	3.96	1.337	2.247	0.082	42.86	0.00616
DD-31	300	150	2.595	3.96	1.481	2.058	0.090	42.93	0.00684
DD-32			0.881	11.01	0.473	10.311	0.031	46.31	0.00250
DD-33			1.754	11.01	1.132	9.818	0.060	35.46	0.00382
DD-34			2.355	11.01	1.263	9.135	0.081	46.37	0.00671
DD-35			2.928	11.01	1.575	8.689	0.102	46.21	0.00831
DD-36			3.495	11.01	1.908	8.286	0.114	45.41	0.00974
DD-37	300	150	1.545	18.15	0.825	16.911	0.060	46.60	0.00442
DD-38			1.800	18.15	0.952	16.691	0.062	47.11	0.00521
DD-39			2.295	18.15	1.235	16.327	0.084	46.19	0.00651
DD-40			2.715	18.15	1.438	15.954	0.103	47.03	0.00784
DD-41			3.300	18.15	1.777	15.530	0.112	46.15	0.00935
DD-42	330	150	1.140	2.96	0.397	1.967	0.028	63.94	0.00365
DD-43			1.365	2.96	0.481	1.549	0.031	62.09	0.00434
DD-44			1.755	2.96	0.618	0.930	0.040	60.48	0.00540
DD-45			2.115	2.96	0.735	0.534	0.047	60.00	0.00646

Table B-5 (Continued)

Run NO.	Reaction		Inlet			Outlet		Conv. CS ₂	Rate -r _{CS₂}
	T (°C)	P _t	P _{CS₂} (kPa _a)	P _{H₂O}	P _{CS₂}	P _{H₂O} (kPa _a)	P _{CO₂}		
DD-46	330	150	0.705	3.96	0.688	2.619	0.034	56.32	0.00545
DD-47			1.575	3.960	0.688	2.619	0.034	56.32	0.00545
DD-48			1.935	3.96	0.911	2.412	0.045	52.92	0.00629
DD-49			2.340	3.96	1.097	2.081	0.052	53.12	0.00763
DD-50			2.595	3.96	1.256	1.936	0.058	51.60	0.00822
DD-51	330	150	0.881	11.01	0.368	10.232	0.021	58.23	0.00315
DD-52			1.754	11.01	0.697	9.406	0.043	60.26	0.00649
DD-53			2.355	11.01	0.963	8.896	0.058	59.11	0.00855
DD-54			2.928	11.01	1.215	8.410	0.069	58.50	0.01052
DD-55			3.495	11.01	1.399	7.829	0.082	59.97	0.01287
DD-56	330	150	1.545	18.15	0.600	16.713	0.038	61.17	0.00580
DD-57			1.800	18.15	0.727	16.518	0.046	59.61	0.00659
DD-58			2.295	18.15	0.905	16.037	0.053	60.57	0.00853
DD-59			2.715	18.15	1.108	15.708	0.069	59.19	0.00987
DD-60			3.300	18.15	1.252	15.036	0.083	62.06	0.01258

Table B-6 Stability of Catalyst Activity (CRS 31)

Time, h	0.25	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
CS ₂										
conv %	83	82.2	80.3	79.9	76.0	75.4	76.2	75.0	75.9	75.0
Time, h	24	25	26	27	28	29	30	31	32	33
CS ₂										
conv %	73	76	76	73.1	73.3	73.1	73.1	73.2	73.1	73.1

Table B-7 Stability of Catalyst Activity (Kaiser 201)

Time, h	0.25	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
CS ₂										
conv %	82	75.2	73.4	71.2	70.0	69.4	71.7	68.0	70.0	66.2
Time, h	24	25	26	27	28	29	30	31	32	33
CS ₂										
conv %	66.1	70	68	67.1	66.4	66.4	66.5	66.3	66.4	66.4

Table B-8 Effect of H₂S and CO₂ on CS₂ Hydrolysis (Kaiser 201)

Feed mol %	Temp. °C	CS ₂ Conversion, %				
		230	255	280	310	340
CS ₂ : 2, H ₂ O: 5.4, N ₂ : 92.6		50.1	61.0	71.6	73.6	75.3
CS ₂ : 2, H ₂ O: 5.4, H ₂ S: 2.2, N ₂ : 90.4		50.8	59.0	69.8	71.1	76.8
CS ₂ : 2, H ₂ O: 5.4, CO ₂ : 2.1, N ₂ : 90.5		52.1	60.0	68.1	71.2	78.0

Table B-9 Effect of H₂S and CO₂ on CS₂ Hydrolysis (CRS 31)

Feed mol %	Temp. °C	CS ₂ Conversion, %				
		230	255	280	310	340
CS ₂ : 2, H ₂ O: 5.4, N ₂ : 92.6		52.1	65.3	80.2	91.4	95.0
CS ₂ : 2, H ₂ O: 5.4, H ₂ S: 2.2, N ₂ : 90.4		53.5	64.9	79.9	90.3	98.0
CS ₂ : 2, H ₂ O: 5.4, CO ₂ : 2.1, N ₂ : 90.5		51.0	64.1	78.1	88.2	95.4

Table B-10 Activity of Promoted Catalysts

Catalyst Comp.	Feed, mol %	Temp., °C	CS ₂ Conversion, %				
			230	255	280	310	340
Kaiser	CS ₂ : 1, H ₂ O: 4,		51.2	59.4	68.0	72.4	77.5
	CS ₂ : 1, H ₂ O: 4, H ₂ S: 2		50.0	60.1	68.2	71.0	77.6
Na/Al ₂ O ₃	CS ₂ : 1, H ₂ O: 4,		31.5	40.0	50.1	58.9	63.1
	CS ₂ : 1, H ₂ O: 4, H ₂ S: 2		34.1	—	49.0	—	61.2
Zn/Al ₂ O ₃	CS ₂ : 1, H ₂ O: 4,		62.5	—	70.0	—	79.1
	CS ₂ : 1, H ₂ O: 4, H ₂ S: 2		59.3	63.1	70.0	75.2	79.0
Cu/Al ₂ O ₃	CS ₂ : 1, H ₂ O: 4,		63.3	—	70.0	—	77.4
	CS ₂ : 1, H ₂ O: 4, H ₂ S: 2		57.1	65.4	69.8	74.2	77.1
Fe/Al ₂ O ₃	CS ₂ : 1, H ₂ O: 4,		74.6	82.0	—	87.5	—
	CS ₂ : 1, H ₂ O: 4, H ₂ S: 2		64.8	76.0	84.9	88.1	—

C. DOCUMENTATION OF EQUATIONS AND PHYSICAL PROPERTIES USED IN THE THESIS

C.1 Derivation of Feed Concentration Setting Equations

C.1.1 CS₂/H₂O/N₂ Feed Setting

The feed compounds, CS₂ and H₂O, were introduced by saturating two streams of nitrogen gases with either H₂O or CS₂ which was held in a 1000 mL glass saturator respectively. The glass saturators were immersed in a water bath or a refrigerated bath respectively. So, for a desired CS₂ or H₂O concentration in feed, flowrate of the two streams of nitrogen gas and bath temperature must be determined.

Assuming that the reaction system is operating at pressure P_t and total flow rate F_t , we have the flowing relationship:

$$F_{s1} = F_{N_2}^1 + F_{CS_2} \quad (C-1)$$

where,

F_{s1} = total flowrate from CS₂ saturator

$F_{N_2}^1$ = N₂ flowrate from CS₂ saturator

F_{CS_2} = CS₂ flowrate from CS₂ saturator

From mass balance, we have:

$$F_{CS_2} = X_{CS_2} F_t \quad (C-2)$$

where,

X_{CS_2} = required mole percent of CS₂ in feed to reactor

In the CS₂ saturator, we have:

$$\frac{P_{CS_2}^0}{P_t} = \frac{P_{CS_2}^0}{P_{N_2}^1 + P_{CS_2}^0} = \frac{F_{CS_2}}{F_{N_2}^1 + F_{CS_2}} \quad (C-3)$$

Rearrangement of (C-3) gives:

$$F_{N_2}^1 = F_{CS_2} \frac{P_t - P_{CS_2}^0}{P_{CS_2}^0} \quad (C-4)$$

Substitution of (C-2) into (C-4) yields:

$$F_{N_2}^1 = X_{CS_2} F_{N_2} \frac{P_t - P_{CS_2}^0}{P_{CS_2}^0} \quad (C-5)$$

Doing mass balance around the H_2O saturator in the same procedure as above, we have the following equation for determine the nitrogen flowrate for saturating H_2O vapor:

$$F_{N_2}^2 = X_{H_2O} F_{N_2} \frac{P_t - P_{H_2O}^0}{P_{H_2O}^0} \quad (C-6)$$

The vapor pressures appearing in equation (C-5) and (C-6) were calculated by the following equations obtained from the regression of data presented in Handbook of Physics and Chemistry (63rd edition, D-196 and D-204).

$$\ln P_{CS_2}^0 = 22.541 - 3521.94/T, \text{ Pa} \quad (C-7)$$

$$\ln P_{H_2O}^0 = 18.871 - 5288.80/T, \text{ Pa} \quad (C-8)$$

The above four equations provide a pre-set of operation condition: water bath temperature, CS_2 refrigerated bath temperature and the two nitrogen flowrates for the desired feed concentration: X_{CS_2} , X_{H_2O} , system pressure and total feed flowrate. A combination of all feed compositions used in the experiments are presented in Table 2.1 of Chapter 2.

C.1.2 $COS/H_2O/N_2$ Feed Setting

In the experiment of COS hydrolysis, H_2O was introduced by saturating nitrogen flow in the same way as described in $CS_2/H_2O/N_2$ feeding system. A 5 %

(vol) COS/N₂ cylinder (obtained from Matheson) was used to introduce COS compound. To regulate the feed compositions, the following mass balance equations were used.

Flowrate from COS/N₂ cylinder:

$$F_{N_2/COS} = \frac{X_{COS} F_t}{5\%} \quad (C-9)$$

N₂ Flowrate for saturating H₂O:

$$F_{N_2} = F_t(1 - X_{H_2O}) - F_{N_2/COS} \quad (C-10)$$

where, X_{H_2O} is the required mole percent of water concentration in feed.

At each required value of water concentration, X_{H_2O} , the water bath temperature was determined by the following equation and equation (C-8).

$$P_{H_2O}^o = P_t \frac{X_{H_2O} F_t}{F_t - F_{N_2/COS}} \quad (C-11)$$

C.2 Estimation of Capillary Condensation of Water and Sulfur

The physical properties of water, sulfur and polysulfur distributions with temperature must be known before capillary condensation can be estimated using the Kelvin equation. Equations (C-12) to (C-17) present the correlations of surface tension, molar volume and vapor pressure of sulfur and water with temperatures (Chemical Engineering Data book of pure chemicals, AIChE). Table C-1 presents the equilibrium distribution of vapor phase polysulfur at different temperatures.

Surface tension:

$$\sigma_s = 0.08603x(1 - T/1313.00)^{1.001}, N/m \quad (C-12)$$

$$\sigma_w = 0.18548 \cdot (1 - T/647.13)^{2.7170 - 3.554 \cdot T + 2.047 \cdot T^2}, N/m \quad (C-13)$$

Molar volume:

$$V_m^s = 0.1044(1 + (1 - T/1313.0)^{0.114}) / 666.4, \text{ m}^3/\text{mol} \quad (\text{C-14})$$

$$V_m^w = 0.3054(1 + (1 - T/647.13)^{0.081}) / 5459, \text{ m}^3/\text{mol} \quad (\text{C-15})$$

Vapor pressure:

$$\ln P_s^0 = 204.74 - 18166/T - 27.433 \ln(T) + 0.017432 \cdot T, \text{ Pa} \quad (\text{C-16})$$

$$\ln P_w^0 = 73.649 - 7258.2/T - 7.3037 \ln(T) + 4.1653e-6 \cdot T^2, \text{ Pa} \quad (\text{C-17})$$

where s and w denote sulfur and water respectively.

Table C-1 Equilibrium Distributions of Polysulfur Compositions

Temp(K)	S ₂	S ₄	S ₆	S ₈
260	0.0	0.0	0.14	0.86
270	0.0	0.0	0.16	0.84
280	0.0	0.0	0.18	0.80
300	0.0	0.0	0.22	0.78
310	0.0	0.0	0.24	0.76
320	0.0	0.0	0.26	0.74
330	0.0	0.0	0.28	0.72
340	0.0	0.0	0.31	0.68
350	0.01	0.0	0.34	0.65

To estimate the affected pore size of the catalyst by sulfur or water condensation at the temperature range from 260 to 350°C, the Kelvin equation (C-18) was used.

$$\ln \frac{P_i}{P_i^0} = \frac{2 \cdot \sigma_i \cdot V_m^i \cos \theta}{RT \cdot r_i}, \quad i = \text{water or sulfur} \quad (\text{C-18})$$

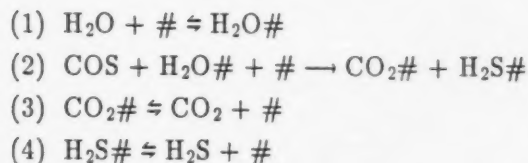
or,

$$r_i = \frac{2 \cdot \sigma_i \cdot V_m^i \cos \theta}{RT \ln P_i / P_i^0}, \quad i = \text{water or sulfur} \quad (\text{C-19})$$

Since the equation involves the partial pressure of sulfur or water in gas phase, a typical condition in LACQ plant Claus unit, 30 vol % water (15 – 30 vol % in Claus unit) and 60 vol % H_2S acid gas, was used during the calculations. The inlet and outlet H_2S concentrations from the Claus first converter were 9.3 mol % and 2.2 mol %, respectively. Assuming that the sulfur produced from converted H_2S was a mixture of polysulfurs in equilibrium. Table C-2 presents the calculation results which is plotted in Figure 3.9 of Chapter 3.

C.3 Derivation of Rate Functions

C.3.1 Rate function of COS hydrolysis according to Eley-Rideal model



where, # represents an active site on catalyst surface.

Assume step (2) to be rate determining, then

$$-r_{\text{CS}_2} = k_2 P_{\text{COS}} [\text{H}_2\text{O}\#] \quad (\text{C-20})$$

The other reactions (step 1, 3 and 4) are assumed to be in equilibrium and thus,

$$K_1 = \frac{[\text{H}_2\text{O}\#]}{P_{\text{H}_2\text{O}} [\#]} \quad (\text{C-21})$$

$$K_3 = \frac{[\#] P_{\text{CO}_2}}{[\text{CO}_2\#]} \quad (\text{C-22})$$

$$K_4 = \frac{[\#] P_{\text{H}_2\text{S}}}{[\text{H}_2\text{S}\#]} \quad (\text{C-23})$$

The total number of active sites available are assumed to be constant 1.

Therefore,

$$1 = [\#] + [\text{H}_2\text{O}\#] + [\text{CO}_2\#] + [\text{H}_2\text{S}\#] \quad (\text{C-24})$$

Substitute equations (C-21) to (C-23) into (C-24) and rearrange,

$$[\#] = \frac{1}{1 + K_1 P_{\text{H}_2\text{O}} + \frac{P_{\text{CO}_2}}{K_3} + \frac{P_{\text{H}_2\text{S}}}{K_4}} \quad (\text{C-25})$$

Solving equations (C-20), (C-21) and (C-25) yields:

$$-r_{\text{COS}} = \frac{k_2 K_1 P_{\text{COS}} P_{\text{H}_2\text{O}}}{1 + K_1 P_{\text{H}_2\text{O}} + \frac{P_{\text{CO}_2}}{K_3} + \frac{P_{\text{H}_2\text{S}}}{K_4}} \quad (\text{C-26})$$

Since the adsorption of CO_2 and H_2S on the surface is negligible compared to that

of H_2O , the rate expression becomes:

$$-r_{\text{cos}} = \frac{k_2 K_1 P_{\text{cos}} P_{H_2O}}{1 + K_1 P_{H_2O}} \quad (\text{C-27})$$

which is the rate function used in Chapter 5.

C.3.2 Rate function of COS hydrolysis according to Langmuir-Hinshelwood

Mechanism

- (1) $H_2O + \# \rightleftharpoons H_2O\#$
- (2) $COS + \# \rightleftharpoons COS\#$
- (3) $COS\# + H_2O\# \rightarrow CO_2\# + H_2S\#$
- (4) $CO_2\# \rightleftharpoons CO_2 + \#$
- (5) $H_2S\# \rightleftharpoons H_2S + \#$

where, # represents active sites on catalyst surface.

Assume step (3) to be rate determining, then

$$-r_{\text{cos}} = k_3 [COS\#] [H_2O\#] \quad (\text{C-28})$$

Using the same derivation procedure as used for equation (C-27), we have the rate expression based on Langmuir-Hinshelwood mechanism:

$$-r_{\text{cos}} = \frac{k_3 K_1 K_2 P_{\text{cos}} P_{H_2O}}{(1 + K_1 P_{H_2O} + K_2 P_{\text{cos}} + \frac{P_{CO_2}}{K_4} + \frac{P_{H_2S}}{K_5})^2} \quad (\text{C-29})$$

Assuming the adsorption of CO_2 and H_2S on the surface is negligible compared to that of H_2O , equation (C-29) becomes:

$$-r_{\text{cos}} = \frac{k_2 K_1 K_2 P_{\text{cos}} P_{H_2O}}{(1 + K_1 P_{H_2O} + K_2 P_{\text{cos}})^2} \quad (\text{C-30})$$

C.3.3 Rate function of COS hydrolysis according to Langmuir-Hinshelwood

Mechanism with two types of surface sites

- (1) $\text{H}_2\text{O} + \#1 \rightleftharpoons \text{H}_2\text{O}\#1$
- (2) $\text{COS} + \#2 \rightleftharpoons \text{COS}\#2$
- (3) $\text{COS}\#2 + \text{H}_2\text{O}\#1 \rightarrow \text{CO}_2\#2 + \text{H}_2\text{S}\#1$
- (4) $\text{CO}_2\#2 \rightleftharpoons \text{CO}_2 + \#2$
- (5) $\text{H}_2\text{S}\#1 \rightleftharpoons \text{H}_2\text{S} + \#1$

where, #1 and #2 represent active site type 1 and 2 on catalyst surface.

Assume step (3) to be rate determining, then

$$-r_{\text{COS}} = k_3 [\text{COS}\#2] [\text{H}_2\text{O}\#1] \quad (\text{C-31})$$

The other reaction steps are assumed to be in equilibrium and thus,

$$K_1 = \frac{[\text{H}_2\text{O}\#1]}{P_{\text{H}_2\text{O}} [\#1]} \quad (\text{C-32})$$

$$K_2 = \frac{[\text{COS}\#2]}{P_{\text{COS}} [\#2]} \quad (\text{C-33})$$

$$K_4 = \frac{[\#2] P_{\text{CO}_2}}{[\text{CO}_2\#2]} \quad (\text{C-34})$$

$$K_5 = \frac{[\#1] P_{\text{H}_2\text{S}}}{[\text{H}_2\text{S}\#1]} \quad (\text{C-35})$$

The total number of active site type 1 or 2 are respectively assumed to be constant

1. Therefore,

$$1 = [\#1] + [\text{H}_2\text{O}\#1] + [\text{H}_2\text{S}\#1] \quad (\text{C-36})$$

and

$$1 = [\#2] + [\text{COS}\#2] + [\text{CO}_2\#2] \quad (\text{C-37})$$

Substitution of (C-32) and (C-35) into (C-36) and, (C-33) and (C-34) into (C-37) respectively yields:

$$[\#1] = \frac{1}{\left(1 + K_1 P_{\text{H}_2\text{O}} + \frac{P_{\text{H}_2\text{S}}}{K_5} \right)} \quad (\text{C-38})$$

and

$$[\#1] = \frac{1}{(1 + K_1 P_{\text{COS}} + \frac{P_{\text{CO}_2}}{K_4})} \quad (\text{C-39})$$

Then, substituting (C-38) and (C-39) into (C-31), we obtain the rate expression:

$$-r_{\text{COS}} = \frac{k_3 K_1 K_2 P_{\text{COS}} P_{\text{H}_2\text{O}}}{(1 + K_1 P_{\text{H}_2\text{O}} + \frac{P_{\text{H}_2\text{S}}}{K_5})(1 + P_{\text{COS}} + \frac{P_{\text{CO}_2}}{K_5})} \quad (\text{C-40})$$

Assuming that the adsorption of the products, CO_2 and H_2S is negligible, we have:

$$-r_{\text{COS}} = \frac{k_3 K_1 K_2 P_{\text{COS}} P_{\text{H}_2\text{O}}}{(1 + K_1 P_{\text{H}_2\text{O}})(1 + K_2 P_{\text{COS}})} \quad (\text{C-41})$$

C.4. Physical Properties of CS_2 and COS Used in the Simulated Claus Process

C.4.1 Viscosity of the gas mixture

The viscosity of a gaseous mixture is calculated from

$$\mu_m = \sum_i \frac{\mu_i}{1 + \sum [\phi_{ij}(y_j/y_i)]} \quad (\text{C-42})$$

where,

$$\phi_{ij} = \frac{[1 + (\mu_i/\mu_j)^{0.5}(M_i/M_j)^{0.25}]^2}{\sqrt{8}(1 + M_i/M_j)^{0.5}} \quad (\text{C-43})$$

$$\phi_{ji} = \mu_j/\mu_i (M_i/M_j) \phi_{ij} \quad (\text{C-44})$$

The viscosity (poise) of the possible species involved in Claus Process at 550 K is:

$$\mu_1 = 0.000225 \quad \mu_2 = 0.000238 \quad \mu_3 = 0.000192 \quad \mu_5 = 0.000272$$

$$\mu_6 = 0.000186 \quad \mu_7 = 0.000227$$

Molecule weight is:

$$M_1 = 34.076 \quad M_2 = 64.060 \quad M_3 = 18.016 \quad M_5 = 28.020$$

$$M_6 = 76.130 \quad M_7 = 60.020$$

where, 1, 2, 3, 5, 6, 7, denote H_2S , SO_2 , H_2O , N_2 , CS_2 and COS .

Thus, equations (C-43), (C-44) yields:

$\phi_{12} = 1.031$	$\phi_{21} = 0.735$	$\phi_{13} = 0.767$	$\phi_{31} = 1.244$
$\phi_{15} = 0.826$	$\phi_{51} = 1.218$	$\phi_{23} = 0.542$	$\phi_{32} = 1.563$
$\phi_{25} = 0.604$	$\phi_{52} = 1.583$	$\phi_{35} = 1.037$	$\phi_{53} = 0.943$
$\phi_{16} = 1.060$	$\phi_{61} = 0.392$	$\phi_{26} = 1.131$	$\phi_{62} = 0.744$
$\phi_{36} = 0.928$	$\phi_{63} = 0.213$	$\phi_{56} = 1.220$	$\phi_{65} = 1.405$
$\phi_{17} = 0.981$	$\phi_{71} = 0.562$	$\phi_{27} = 1.024$	$\phi_{72} = 1.042$
$\phi_{37} = 0.876$	$\phi_{73} = 0.311$	$\phi_{57} = 1.078$	$\phi_{75} = 1.922$
$\phi_{67} = 2.077$	$\phi_{76} = 3.216$		

For a Claus gas with an average composition of 10 mol % H_2S , 5 mol % SO_2 , 20 mol % H_2O , 0.05 mol % CS_2 , 0.04 mol % COS and 64.91 mol % N_2 , equation (C-42) gives the mixture viscosity:

$$\mu_m = 0.000129 \text{ poise}$$

C.4.2 Molecular Diffusivity

To evaluate the molecular diffusivity of the species in the Claus process, the Wilke and Lee modification of the equation by Hirschfelder, Bird and Spotz is used (Chemical Engineers' Handbook, Perry and Chilton, 5th edition, 3-231).

$$D_{b1,2} = \frac{B T^{1.5} (1/M_1 + 1/M_2)^{0.5}}{P \sigma_{12}^2 \Omega} \quad (\text{C-45})$$

Where,

$$B = [10.85 - 2.50 (1/M_1 + 1/M_2)^{0.5}] \times 10^{-4}$$

Ω = collision integral; function of kT/ϵ_{12}

σ_{12} , ϵ_{12} = constants in the Lennard-Jones potential energy function for the

molecular pair 1 and 2; σ is in Å.

The multi-component diffusivity was then calculated by equation (C-46):

$$\frac{1}{D_{bjm}} = \frac{\sum \left(\frac{1}{D_{bjk}} \right) (y_k - y_j) a_k / a_j}{1 - y_j \sum a_k / a_j} \quad (C-46)$$

For 550 K, 1 atm, equation (C-42) gives the binary bulk diffusivities in cm^2/sec as,

$D_{b12} = 0.302$	$D_{b13} = 0.521$	$D_{b15} = 0.104$	$D_{b16} = 0.051$
$D_{b17} = 0.073$	$D_{b23} = 0.406$	$D_{b25} = 0.074$	$D_{b26} = 0.041$
$D_{b27} = 0.054$	$D_{b35} = 0.131$	$D_{b36} = 0.101$	$D_{b37} = 0.134$
$D_{b56} = 0.056$	$D_{b57} = 0.073$	$D_{b67} = 0.0504$	

At mean composition of 10 mol % H_2S , 5 mol % SO_2 , 20 mol % H_2O , 0.05 mol % CS_2 , 0.04 mol % COS and 64.91 mol % N_2 , equation (C-46) gives:

$$D_{b6m} = 0.0604$$

$$D_{b7m} = 0.0789$$

C.4.3 Film diffusivity

The theoretical calculation of film mass transfer coefficient, k_m , is shown below:

$$j_D = \frac{k_m \rho_m}{G} S_c^{2/3} = \frac{0.25}{R_e^{0.41} - 0.15} \quad (C-47)$$

$$\text{or } k_m = \frac{G}{\rho_m S_c^{2/3}} \times \frac{0.25}{R_e^{0.41} - 0.15} \quad (C-48)$$

where,

D_p — particle diameter, m

R_e — Reynolds number = $\frac{G D_p}{\mu_m}$

G — superficial velocity, $\text{kg}/\text{m}^2 \text{ s}$

ρ_m — density of gas mixture, kg/m^3

D_{bjm} — molecular diffusivity coefficient, m^2/s

C.4.4 Knudsen Diffusivity

The Knudsen diffusivity of the Claus species is calculated from

$$D_{kj} = 9.7 \times 10^{-3} \bar{r}_p (T/M_j)^{0.5} \quad (C-49)$$

where $\bar{r}_p$ = average of radius of a pore = 3 nm for alumina Kaiser 201

Then, at 550 K

$$D_{k6} = 0.078, \text{ cm}^2/\text{s} \quad D_{k7} = 0.088 \text{ cm}^2/\text{s}$$

The effective diffusivity in catalyst pore can be calculated by

$$D_{ej} = \varepsilon/\tau D_{kj} \quad (C-50)$$

where, ε = catalyst porosity = 0.6604 for alumina(Kaiser 201), τ = catalyst tortuosity.

Substituting the recommended value of $\tau = 4$ in equation (C-50) gives:

$$D_{e6} = 0.013 \quad D_{e7} = 0.015$$

D FORTRAN PROGRAM

D.1 NONLINEAR REGRESSION PROGRAM

This appendix contains a mainline "NONLREG.FOR" and fifteen subroutines which enable the fitting of a nonlinear model to a data set and the subsequent investigation of the properties of the parameter estimators for that model/data set combination. An example input and output, illustrating the use of the program, is also attached at the end of the program when implemented on the Mainframe MTS. Some features of the routines are as follows:

1. The subroutine "EVAL" called in the mainline can be one of the EVAL1, EVAL2 ..., and EVAL7. In the example input and output illustration of the use of the the program "NONLREG.FOR", the subroutine "EVAL7" was called.
2. Most of the subroutines used in NONLREG.FOR are updated from program "NONLIN" in the book "Nonlinear Regression Modeling" (David 1983) which was designed to be used on a CDC Cyber 76 computer.
3. Subroutine RNSET which generates uniform pseudo-random number is available on MTS in *IMSLSTATS subroutine library.
4. The program requires access to a number of subroutines from the LINPACK packages which is available on MTS in *LINPACK library.


```

*****
C          MAINLINE "NONLREG.FOR"
C  THIS PROGRAM ANALYZES KINETIC DATA TO OBTAIN PARAMETERS
C  FOR THE MODEL/DATA SET COMBINATION AND TO EXAMINE THE
C  PROPERTIES OF THE PARAMETER ESTIMATES.
C *****
C  JPVT(K) = K.GE.NP, USED TO RECORD COLUMN INTERCHANGES
C          DURING THE QR DECOMPOSITION
C  NPTS = THE NUMBER OF OBSERVATIONS
C  NP = THE NUMBER OF PARAMETERS
C  NITS = THE MAXIMUM NUMBER OF ITERATIONS ALLOWED
C  ND1 = THE LEADING DIMENSION OF THE MATRIX VARC
C  VARC(ND1,K) = ND1.GE.NP K.GE.NP, THE PARAMETER
C          VARIANCE-COVARIANCE MATRIX
C  JOB = PRINT OPTIONS
C  NSIM = SIMULATION NUMBER ( USE 1000 IN THIS PROGRAM)
C  IFAIL = ERROR INDICATOR
C  Y(K) = K .GE. NPTS, THE NPTS VALUE OF THE DEPENDENT VARIABLE
C  PARAM(K) = K.GE.NP, THE INITIAL ESTIMATES OF THE NP
C  PARAMETERS THE VALUES OF PARAMETERS AT CONVERGENCE OR
C  AT THE FINAL ITERATION IF CONVERGENCE WAS NOT ACHIEVED
C  DERIVS(K) = K.GE.NPTS*NP, USED INITIALLY TO STORE THE
C          FIRST-ORDER DERIVATIVES AND LATER TO STORE
C          COMPONENTS OF THE QR DECOMPOSITION
C  A(K) = K.GE.NPTS*NP*NP, WORKING STORAGE, USED INITIALLY TO
C          STORE THE SECOND-ORDER PARTIAL DERIVATIVES AND LATER
C          THE ACCELERATION ARRAY
C  QRAUX(K) = K.GE.NP, USED TO STORE INFORMATION FROM TH EQR
C          DECOMPOSITION
C  WK1(K) = K.GE.NP*(NP+1)/2, A GENERAL WORKING VECTOR
C  WK2(K) = K.GE.NPTS, ATEMPORARY STORAGE VECTOR USED ONLY IN
CC  SUBROUTINE CURVE
C  DIFF(K) = K.GE.NPTS, USED TO STORE THE VECTOR OF DIFFERENCES
C          BETWEEN ACTUAL AND FITTED VALUES
C  BIAS(K) = K.GE.NP, BOX'S ESTIMATE OF BIAS FOR EACH OF THE
C          PARAMETERS
C  STMATE(K,4) = K.GE.NSIM,
C  ALPHA = THE CONVERGENCE CRITERION, IF THE ABSOLUTE VALUE
C          OF THE RATIO OF THE PARAMETER CORRECTION TO THE
C          PARAMETER VALUE DOES NOT EXCEED ALPHA FOR ALL PARAMETERS
C          THEN CONVERGENCE IS CONSIDERED TO HAVE OCCURED
C  SEED = REQUIRED BY THE PSEUDO-RANDOM NUMBER GENERATOR
C          RNSET OF MAINFRAM MTS
C  RSS = THE RESIDUAL SUM OF SQUARES FROM THE LAST ITERATION
C  VAR = THE RESIDUAL VARIANCE AT CONVERGENCE
C  SD = TH EERROR COMPONENTS ARE TO BE GENERATED FROM A
C          POPULATION WITH A STANDARD DEVIATION OF SD
C          EXTERNAL EVAL
C  EVAL CAN BE ANY ONE OF EVAL1, EVAL2, ---, OR EVAL7 SUBROUTINES
C  WHICH IS SUPPLIED BY USER TO CALCULATE PREDICTED VALUES FOR A
C  MODEL
C          INTEGER JPVT(2),LUNIN,LUNOUT,NPTS,NP,NITS,ND1,I,J,JOB,NSIM,NS,

```

```

+ IFAIL
  REAL Y(60),PARAM(3),PAR(3),VARC(3,3),DERIVS(180),A(540),
+ WK1(6),WK2(60),DIFF(60),BIAS(3),STMATE(1000,4),X,ALPHA,SEED,
+ RSS,VAR,SD,FLOAT,SQRT,ALOG,X2,QRAUX(3)
  COMMON X(60),X2(60)
  DATA NITS/200/,ND1/2/
  DATA ALPHA/0.57/
  DATA SEED/2.962357E0/
  WRITE(6,10)
  WRITE(6,*)'ENTER HOW MANY PARAMETERS TO BE ESTIMATED IN
& YOUR FUNCTION'
  READ(5,*)NP
  WRITE(6,*)'ENTER HOW MANY OBSERVATIONS YOU HAVE'
  READ(5,*)NPTS
  WRITE(5,*)'ENTER INITIAL GUESS OF THE PARAMETERS'
  READ(5,*)(PARAM(I),I=1,NP)
  DO 100 I=1,NPTS
  READ(8,*)X(I),X2(I),Y(I)
  X(I)=X(I)*1.5
  X2(I)=X2(I)*1.5
  WRITE(6,30)X(I),X2(I),Y(I)
100  CONTINUE
  JOB=11111
  CALL SOLVE(Y,PARAM,ALPHA,NITS,NPTS,NP,ND1,LUNOUT,JOB,EVAL,
+  VARC,RSS,IFAIL,DERIVS,QRAUX,JPVT,DIFF,WK1)
  IF(IFAIL.NE.0)STOP
  JOB=111
  VAR=RSS/FLOAT(NPTS-NP)
  CALL BATES(PARAM,VAR,NITS,NPTS,NP,LUNOUT,JOB,EVAL,BIAS,IFAIL,
+  A,DERIVS,VARC,QRAUX,WK1,WK2,JPVT)
  IF(IFAIL.NE.0)STOP
  NSIM=1000
  JOB=1001
  IF(NSIM.GT.10)JOB=0
  SD=SQRT(VAR)
  CALL RNSET(SEED)
  DO 200 I=1,NSIM
  DO 300 J=1,NP
  PAR(J)=PARAM(J)
300  CONTINUE
  CALL GNRATE(PAR,SD,NPTS,LUNOUT,EVAL,Y,IFAIL)
  CALL SOLVE(Y,PAR,ALPHA,NITS,NPTS,NP,ND1,LUNOUT,JOB,EVAL,
+  VARC,RSS,IFAIL,DERIVS,QRAUX,JPVT,DIFF,WK1)
  IF(IFAIL.NE.0)STOP
  DO 400 J=1,NP
  STMATE(I,J)=PAR(J)
400  CONTINUE
200  CONTINUE
  JOB=11
  DO 500 I=1,NP
  WRITE(LUNOUT,40)I
  CALL SUMRY(STMATE(1,I),NSIM,LUNOUT,JOB,IFAIL)

```

```

500 CONTINUE
STOP
10 FORMAT(///1H ,10X,20HLEAF PRODUCTION DATA
+ //1H ,9X,1HX,9X,1HY//)
20 FORMAT(F10.5,F10.5)
30 FORMAT(1H ,5X,F10.5,5X,F10.5,5X,F10.5)
40 FORMAT(///1H ,10X,13HPARAMTER NO.,I4)
END

C
SUBROUTINE EVAL1(PARAM,I,ITASK,WK1,IFAIL)
*****
C THIS SUBROUTINE EVALUATES THE FIRST AND SECOND ORDER
C PARTIAL DERIVATIVES FOR THE ELEY-RIDEAL MODEL:
C RATE=PARAM(1)*PARAM(2)*X(I)*X2(I)/(1+PARAM(2)*X2(I))
*****
C WK1(K) = K.GE.NP*(NP+1)/2
C FIRST DERIVATIVE, WK1(1)=D(1),WK1(2)=D(2).....WK1(NP)=D(NP)
C SECOND DERIVATIVE, WK1(1)=D(1,1), WK1(2)=D(2,1), WK1(3)=D(2,2)
C WK1(4)=D(3,1), WK1(5)=D(3,2), WK1(6)=D(3,3), WK1(7)=D(4,1), .....,
C WK1(NP*(NP+1)/2)=D(NP,NP)
INTEGER I,ITASK,IFAIL
REAL PARAM(2),WK1(3),X,X2,ZERO,ONE,TWO
COMMON X(60),X2(60)
DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
IFAIL=0
IF(ITASK.NE.0)GO TO 1111
WK1(1)=PARAM(1)*PARAM(2)*X(I)*X2(I)/(1+PARAM(2)*X2(I))
RETURN
1111 CONTINUE
IF(ITASK.NE.1)GO TO 2222
WK1(1)=PARAM(2)*X(I)*X2(I)/(1+PARAM(2)*X2(I))
WK1(2)=PARAM(1)*X(I)*X2(I)/(1+PARAM(2)*X2(I))**2
RETURN
2222 CONTINUE
IF(ITASK.NE.2)GO TO 3333
WK1(1)=ZERO
WK1(2)=X(I)*X2(I)/(1+PARAM(2)*X2(I))**2
WK1(3)=-2*PARAM(1)*X(I)*X2(I)**2/(1+PARAM(2)*X2(I))**3
RETURN
3333 CONTINUE
IFAIL=1
RETURN
END

C
SUBROUTINE EVAL2(PARAM,I,ITASK,WK1,IFAIL)
*****
C THIS SUBROUTINE EVALUATES THE FIRST AND SECOND ORDER
C PARTIAL DERIVATIVES FOR THE MODIFIED ELEY-RIDEAL MODEL:
C RATE=PARAM(1)*PARAM(2)*X(I)*X2(I)/
C (1+PARAM(2)*X2(I))**PARAM(3)
*****
C WK1(K) = K.GE.NP*(NP+1)/2

```

```

C FIRST DERIVATIVE, WK1(1)=D(1),WK1(2)=D(2).....WK1(NP)=D(NP)
C SECOND DERIVATIVE, WK1(1)=D(1,1), WK1(2)=D(2,1), WK1(3)=D(2,2)
C WK1(4)=D(3,1), WK1(5)=D(3,2), WK1(6)=D(3,3), WK1(7)=D(4,1), .....,
C WK1(NP*(NP+1)/2)=D(NP,NP)
  INTEGER I,ITASK,IFAIL
  REAL PARAM(3),WK1(6),X,X2,ZERO,ONE,TWO
  COMMON X(60),X2(60)
  DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
  IFAIL=0
  IF(ITASK.NE.0)GO TO 1111
  WK1(1)=PARAM(1)*PARAM(2)*X(I)*X2(I)/(ABS(1+PARAM(2)*X2(I))
+ ) **PARAM(3)
  RETURN
1111 CONTINUE
  IF(ITASK.NE.1)GO TO 2222
  WK1(1)=PARAM(2)*X(I)*X2(I)/(ABS(1+PARAM(2)*X2(I)))**PARAM(3)
  WK1(2)=PARAM(1)*X(I)*X2(I)/(ABS(1+PARAM(2)*X2(I)))**PARAM(3)
+ -PARAM(3)*PARAM(1)*PARAM(2)*X(I)*X2(I)**2/(ABS(1+PARAM(2)*
+ X2(I)))**PARAM(3)+1)
  WK1(3)=-PARAM(1)*PARAM(2)*X(I)*X2(I)*ALOG(ABS(1+PARAM(2)
+ *X2(I))) /(ABS(1+PARAM(2)*X2(I)))**PARAM(3)
  RETURN
2222 CONTINUE
  IF(ITASK.NE.2)GO TO 3333
  WK1(1)=ZERO
  WK1(2)=X(I)*X2(I)/(ABS(1+PARAM(2)*X2(I)))**PARAM(3)
+ -PARAM(3)*PARAM(2)*X(I)*X2(I)**2/(ABS(1+PARAM(2)*
+ X2(I)))**PARAM(3)+1)
  WK1(3)=-2*PARAM(3)*PARAM(1)*X(I)*X2(I)**2/(ABS(1+PARAM(2)
+ *X2(I)))**PARAM(3)+1)+PARAM(3)*(PARAM(3)+1)*PARAM(1)
+ *PARAM(2)*X(I)*X2(I)**3/(ABS(1+PARAM(2)*X2(I)))**PARAM(3)+2)
  WK1(4)=-PARAM(2)*X(I)*X2(I)*ALOG(ABS(1+PARAM(2)*X2(I)))
+ /(ABS(1+PARAM(2)*X2(I)))**PARAM(3)
  WK1(5)=-PARAM(1)*X(I)*X2(I)*ALOG(ABS(1+PARAM(2)*X2(I)))
+ /(ABS(1+PARAM(2)*X2(I)))**PARAM(3)-PARAM(1)*PARAM(2)
+ *X(I)*X2(I)**2/(ABS(1+PARAM(2)*X2(I)))**PARAM(3)+1)+PARAM(3)*
+ PARAM(1)*PARAM(2)*X(I)*X2(I)**2*ALOG(ABS(1+PARAM(2)*X2(I)))/
+ (ABS(1+PARAM(2)*X2(I)))**PARAM(3)+1)
  WK1(6)=PARAM(1)*PARAM(2)*X(I)*X2(I)*(ALOG(1+PARAM(2)*X2(I)))
+ **2/(ABS(1+PARAM(2)*X2(I)))**PARAM(3)
  RETURN
3333 CONTINUE
  IFAIL=1
  RETURN
END

```

C

```

      SUBROUTINE EVAL3(PARAM,I,ITASK,WK1,IFAIL)
C *****
C THIS SUBROUTINE EVALUATES THE FIRST AND SECOND ORDER
C PARTIAL DERIVATIVES FOR THE LANGMUIR-HINSHLWOOD MODEL (1):
C RATE=PARAM(1)*PARAM(2)*PARAM(3)*X(I)*X2(I)/
C (1+PARAM(2)*X(I)+PARAM(3)*X2(I))**2
C *****
C WK1(K) = K.GE.NP*(NP+1)/2
C WK1(1)=PARAM(1)*PARAM(2)*PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I)+
C FIRST DERIVATIVE, WK1(1)=D(1),WK1(2)=D(2).....WK1(NP)=D(NP)
C SECOND DERIVATIVE, WK1(1)=D(1,1), WK1(2)=D(2,1), WK1(3)=D(2,2)
C WK1(4)=D(3,1), WK1(5)=D(3,2), WK1(6)=D(3,3), WK1(7)=D(4,1), .....,
C WK1(NP*(NP+1)/2)=D(NP,NP)
      INTEGER I,ITASK,IFAIL
      REAL PARAM(3),WK1(6),X,X2,ZERO,ONE,TWO
      COMMON X(60),X2(60)
      DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
      IFAIL=0
      IF(ITASK.NE.0)GO TO 1111
      WK1(1)=PARAM(1)*PARAM(2)*PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I)+
+ PARAM(3)*X2(I))**2
      RETURN
1111  CONTINUE
      IF(ITASK.NE.1)GO TO 2222
      WK1(1)=PARAM(2)*PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I)+
+ PARAM(3)*X2(I))**2
      WK1(2)=PARAM(1)*PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I)+
+ PARAM(3)*X2(I))**2
      + -2*PARAM(3)*PARAM(1)*PARAM(2)*X(I)**2*X2(I)/(1+PARAM(2)*
+ X(I)+PARAM(3)*X(I))**3
      WK1(3)=PARAM(1)*PARAM(2)*X(I)*X2(I)/(1+PARAM(2)*X(I)+
+ PARAM(3)*X2(I))**2-2*PARAM(3)*PARAM(1)*PARAM(2)**2/
+ (1+PARAM(2)*X(I)+PARAM(3)*X2(I))**3
      RETURN
2222  CONTINUE
      IF(ITASK.NE.2)GO TO 3333
      WK1(1)=ZERO
      WK1(2)=PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I)+PARAM(3)*X2(I))**2
      + -2*PARAM(2)*PARAM(3)*X(I)**2*X2(I)/(1+PARAM(2)*
+ X(I)+PARAM(3)*X2(I))**3
      WK1(3)=-4*PARAM(3)*PARAM(1)*X(I)**2*X2(I)/(1+PARAM(2)
+ *X(I)+PARAM(3)
      + *X2(I))**3+6*PARAM(1)*PARAM(2)*PARAM(3)*X(I)**3*X2(I)/
      + (1+PARAM(2)*X(I)+PARAM(3)*X2(I))**4
      WK1(4)=PARAM(2)*X(I)*X2(I)/(1+PARAM(2)*X(I)+PARAM(3)*X2(I))**2
      + -2*PARAM(2)*PARAM(3)*X(I)*X2(I)**2/(1+PARAM(2)*
      + X(I)+PARAM(3)*X2(I))**3
      WK1(5)=PARAM(1)*X(I)*X2(I)/(1+PARAM(2)*X(I)+PARAM(3)
      + *X2(I))**2-2*PARAM(1)*PARAM(2)*X(I)**2*X2(I)/
      + (1+PARAM(2)*X(I)+PARAM(3)*X2(I))**3-2*PARAM(1)*PARAM(3)*X(I)*
      + X2(I)**2/(1+PARAM(2)*X(I)+PARAM(3)*X2(I))**3+6*PARAM(3)*
      + PARAM(1)*PARAM(2)*X(I)**2*X2(I)**2/(1+PARAM(2)*X(I)+PARAM(3)

```



```

+ *X2(I)**4
  WK1(6)=-4*PARAM(1)*PARAM(2)*X(I)*X2(I)**2/
+ (1+PARAM(2)*X(I)+PARAM(3)*X2(I))**3+6*PARAM(3)*PARAM(1)
+ *PARAM(2)*X(I)*X2(I)**3/(1+PARAM(2)*X(I)+PARAM(3)*X2(I))**4
  RETURN
3333 CONTINUE
  IFAIL=1
  RETURN
  END

C
  SUBROUTINE EVAL4(PARAM,I,ITASK,WK1,IFAIL)
C *****
C THIS SUBROUTINE EVALUATES THE FIRST AND SECOND ORDER
C PARTIAL DERIVATIVES FOR THE LANGMUIR-HINSHLWOOD MODEL (2):
C RATE=PARAM(1)*PARAM(2)*PARAM(3)*X(I)*X2(I)/
C ((1+PARAM(2)*X(I))*(1+PARAM(3)*X2(I)))
C *****
C WK1(K) = K.GE.NP*(NP+1)/2
C FIRST DERIVATIVE, WK1(1)=D(1),WK1(2)=D(2).....WK1(NP)=D(NP)
C SECOND DERIVATIVE, WK1(1)=D(1,1), WK1(2)=D(2,1), WK1(3)=D(2,2)
C WK1(4)=D(3,1), WK1(5)=D(3,2), WK1(6)=D(3,3), WK1(7)=D(4,1), .....,
C WK1(NP*(NP+1)/2)=D(NP,NP)
  INTEGER I,ITASK,IFAIL
  REAL PARAM(3),WK1(6),X,X2,ZERO,ONE,TWO
  COMMON X(60),X2(60)
  DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
  IFAIL=0
  IF(ITASK.NE.0)GO TO 1111
  WK1(1)=PARAM(1)*PARAM(2)*PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I))/
+ (1+PARAM(3)*X2(I))
  RETURN
1111 CONTINUE
  IF(ITASK.NE.1)GO TO 2222
  WK1(1)=PARAM(2)*PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I))
+ /(1+PARAM(3)*X2(I))
  WK1(2)=PARAM(1)*PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I))**2
+ /(1+PARAM(3)*X2(I))
  WK1(3)=PARAM(1)*PARAM(2)*X(I)*X2(I)/(1+PARAM(2)*X(I))/
+ (1+PARAM(3)*X2(I))**2
  RETURN
2222 CONTINUE
  IF(ITASK.NE.2)GO TO 3333
  WK1(1)=ZERO
  WK1(2)=PARAM(3)*X(I)*X2(I)/(1+PARAM(2)*X(I))**2/
+ (1+PARAM(3)*X2(I))
  WK1(3)=-2*PARAM(1)*PARAM(3)*X(I)**2*X2(I)/
+ (1+PARAM(2)*X(I))**3/(1+PARAM(3)*X2(I))
  WK1(4)=PARAM(2)*X(I)*X2(I)/(1+PARAM(2)*X(I))/
+ (1+PARAM(3)*X2(I))**2
  WK1(5)=PARAM(1)*X(I)*X2(I)/(1+PARAM(2)*X(I))**2/
+ (1+PARAM(3)*X2(I))**2
  WK1(6)=-2*PARAM(1)*PARAM(2)*X(I)*X2(I)**2/

```



```

      + (1+PARAM(2)*X(I))/(1+PARAM(3)*X2(I))**3
      RETURN
3333  CONTINUE
      IFAIL=1
      RETURN
      END

      SUBROUTINE EVAL5(PARAM,I,ITASK,WK1,IFAIL)
C *****
C THIS SUBROUTINE EVALUATES THE FIRST AND SECOND ORDER
C PARTIAL DERIVATIVES FOR THE REPARAMETERIZED ELEY RIDEAL MODEL:
C RATE=PARAM(1)*X(I)*X2(I)/(1+PARAM(2)*X2(I))
C *****
C WK1(K) = K.GE.NP*(NP+1)/2
C FIRST DERIVATIVE, WK1(1)=D(1),WK1(2)=D(2).....WK1(NP)=D(NP)
C SECOND DERIVATIVE, WK1(1)=D(1,1), WK1(2)=D(2,1), WK1(3)=D(2,2)
C WK1(4)=D(3,1), WK1(5)=D(3,2), WK1(6)=D(3,3), WK1(7)=D(4,1), .....,
C WK1(NP*(NP+1)/2)=D(NP,NP)
      INTEGER I,ITASK,IFAIL
      REAL PARAM(2),WK1(3),X,X2,ZERO,ONE,TWO
      COMMON X(60),X2(60)
      DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
      IFAIL=0
      IF(ITASK.NE.0)GO TO 1111
      WK1(1)=PARAM(1)*X(I)*X2(I)/(1+PARAM(2)*X2(I))
      RETURN
1111  CONTINUE
      IF(ITASK.NE.1)GO TO 2222
      WK1(1)=X(I)*X2(I)/(1+PARAM(2)*X2(I))
      WK1(2)=-PARAM(1)*X(I)*X2(I)**2/(1+PARAM(2)*X2(I))**2
      RETURN
2222  CONTINUE
      IF(ITASK.NE.2)GO TO 3333
      WK1(1)=ZERO
      WK1(2)=-X(I)*X2(I)**2/(1+PARAM(2)*X2(I))**2
      WK1(3)=2*PARAM(1)*X(I)*X2(I)**3/(1+PARAM(2)*X2(I))**3
      RETURN
3333  CONTINUE
      IFAIL=1
      RETURN
      END

C
      SUBROUTINE EVAL6(PARAM,I,ITASK,WK1,IFAIL)
C *****
C THIS SUBROUTINE EVALUATES THE FIRST AND SECOND ORDER
C PARTIAL DERIVATIVES FOR THE REPARAMETERIZED ELEY RIDEAL
C MODEL:
C RATE=param(1)*X(I)*X2(I)/(PARAM(2)+X2(I))
C *****
C WK1(K) = K.GE.NP*(NP+1)/2
C FIRST DERIVATIVE, WK1(1)=D(1),WK1(2)=D(2).....WK1(NP)=D(NP)
C SECOND DERIVATIVE, WK1(1)=D(1,1), WK1(2)=D(2,1), WK1(3)=D(2,2)

```

```

C WK1(4)=D(3,1), WK1(5)=D(3,2), WK1(6)=D(3,3), WK1(7)=D(4,1), .....,
C WK1(NP*(NP+1)/2)=D(NP,NP)
  INTEGER I,ITASK,IFAIL
  REAL PARAM(2),WK1(3),X,X2,ZERO,ONE,TWO
  COMMON X(60),X2(60),Y(60)
  DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
  IFAIL=0
  IF(ITASK.NE.0)GO TO 1111
  WK1(1)=param(1)*X(I)*X2(I)/(PARAM(2)+X2(I))
  RETURN
1111 CONTINUE
  IF(ITASK.NE.1)GO TO 2222
  WK1(1)=X(I)*X2(I)/(PARAM(2)+X2(I))
  WK1(2)=-param(1)*X(I)*X2(I)/(PARAM(2)+X2(I))**2
  RETURN
2222 CONTINUE
  IF(ITASK.NE.2)GO TO 3333
  WK1(1)=0.0
  WK1(2)=-X(I)*X2(I)/(PARAM(2)+X2(I))**2
  WK1(3)=2*param(1)*X(I)*X2(I)/(PARAM(2)+X2(I))**3
  RETURN
3333 CONTINUE
  IFAIL=1
  RETURN
END

C
  SUBROUTINE EVAL7(PARAM,I,ITASK,WK1,IFAIL)
C *****
C THIS SUBROUTINE EVALUATES THE FIRST AND SECOND ORDER
C PARTIAL DERIVATIVES FOR THE REPARAMETERIZED ELEY RIDEAL
C MODEL:
C RATE=X(I)*X2(I)/(PARAM(1)+PARAM(2)*X2(I))
C *****
C WK1(K) = K.GE.NP*(NP+1)/2
C FIRST DERIVATIVE, WK1(1)=D(1),WK1(2)=D(2).....WK1(NP)=D(NP)
C SECOND DERIVATIVE, WK1(1)=D(1,1), WK1(2)=D(2,1), WK1(3)=D(2,2)
C WK1(4)=D(3,1), WK1(5)=D(3,2), WK1(6)=D(3,3), WK1(7)=D(4,1), .....,
C WK1(NP*(NP+1)/2)=D(NP,NP)
  INTEGER I,ITASK,IFAIL
  REAL PARAM(2),WK1(3),X,X2,ZERO,ONE,TWO
  COMMON X(60),X2(60),Y(60)
  DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
  IFAIL=0
  IF(ITASK.NE.0)GO TO 1111
  WK1(1)=X(I)*X2(I)/(PARAM(1)+PARAM(2)*X2(I))
  RETURN
1111 CONTINUE
  IF(ITASK.NE.1)GO TO 2222
  WK1(1)=-X(I)*X2(I)/(PARAM(1)+PARAM(2)*X2(I))**2
  WK1(2)=-X(I)*X2(I)**2/(PARAM(1)+PARAM(2)*X2(I))**2
  RETURN
2222 CONTINUE

```

```

      IF(ITASK.NE.2)GO TO 3333
      WK1(1)=2*X(I)*X2(I)/(PARAM(1)+PARAM(2)*X2(I))**3
      WK1(2)=2*X(I)*X2(I)**2/(PARAM(1)+PARAM(2)*X2(I))**3
      WK1(3)=2*X(I)*X2(I)**3/(PARAM(1)+PARAM(2)*X2(I))**3
      RETURN
3333  CONTINUE
      IFAIL=1
      RETURN
      END
C
      SUBROUTINE SOLVE(Y,PARAM,ALPHA,NITS,NPTS,NP,ND1,LUNOUT,
+ JOB,EVAL, VARC,RSS,IFAIL,DERIVS,QRAUX,JPVT,DIFF,WK1)
C *****
C  SUBROUTINE SOLVE ESTIMATES THE PARAMETERS FOR A NONLINEAR
C  SYSTEM THE GAUSS-NEWTON METHOD
C *****
      EXTERNAL EVAL
      INTEGER JPVT(1), IFAIL,NPTS, NP,NITS,ND1,LUNOUT,JOB,
+      I,J,K,L,ITER,ITASK
      REAL DERIVS(NPTS,1),VARC(ND1,1),Y(1),PARAM(1),DIFF(1),
+ WK1(1),QRAUX(1),DUM(1), ALPHA,RSS,RES,TEST,RESVAR,
+ ACCUM,DENOM,ABS,FLOAT,ZERO,ONE
      LOGICAL CNVRGD,PRNPAR
      DATA ZERO/0.0E0/,ONE/1.0E0/
      IFAIL=0
      PRNPAR=JOB/1000.NE.0
      IF(.NOT.PRNPAR)GO TO 1111
      WRITE(LUNOUT,10)(I,I=1,NP)
      RSS=ZERO
      DO 100 I=1,NPTS
      ITASK=0
      CALL EVAL(PARAM,I,ITASK,WK1,IFAIL)
      IF(IFAIL.NE.0)GO TO 6666
      RES=Y(I)-WK1(1)
      RSS=RSS+RES*RES
100  CONTINUE
      WRITE(LUNOUT,20)RSS,(PARAM(I),I=1,NP)
1111  CONTINUE
      ITER=1
2222  CONTINUE
      DO 200 I=1,NPTS
      ITASK=0
      CALL EVAL(PARAM,I,ITASK,WK1,IFAIL)
      IF(IFAIL.NE.0)GO TO 6666
      DIFF(I)=Y(I)-WK1(1)
      ITASK=1
      CALL EVAL(PARAM,I,ITASK,WK1,IFAIL)
      IF(IFAIL.NE.0)GO TO 6666
      DO 300 J=1,NP
      DERIVS(I,J)=WK1(J)
300  CONTINUE
200  CONTINUE

```

```

DO 400 I=1,NP
JPVT(I)=0
400  CONTINUE
CALL SQRDC(DERIVS,NPTS,NPTS,NP,QRAUX,JPVT,WK1,1)
CALL SQRSL(DERIVS,NPTS,NPTS,NP,QRAUX,DIFF,DUM,DIFF,WK1,DUM,
+ DUM,100,IFAIL)
IF(IFAIL.NE.0)GO TO 5555
CNVRGD=.TRUE.
DO 500 I=1,NP
J=JPVT(I)
PARAM(J)=PARAM(J)+WK1(I)
DENOM=PARAM(J)
IF(DENOM.EQ.ZERO)DENOM=ONE
TEST=WK1(I)/DENOM
IF(ABS(TEST).GT.ALPHA)CNVRGD=.FALSE.
500  CONTINUE
RSS=ZERO
DO 600 I=1,NPTS
ITASK=0
CALL EVAL(PARAM,I,ITASK,WK1,IFAIL)
IF(IFAIL.NE.0)GO TO 6666
RES=Y(I)-WK1(1)
RSS=RSS+RES*RES
600  CONTINUE
IF(.NOT.PRNPARGO TO 3333
WRITE(LUNOUT,20)RSS,(PARAM(I),I=1,NP)
3333  CONTINUE
ITER=ITER+1
IF(ITER.GT.NITS)GO TO 4444
IF(.NOT.CNVRGD)GO TO 2222
IF(NPTS.EQ.NP)GO TO 7777
CALL STRDI(DERIVS,NPTS,NP,DUM,011,IFAIL)
IF(IFAIL.NE.0)GO TO 5555
RESVAR=RSS/FLOAT(NPTS-NP)
DO 700 I=1,NP
DO 800 J=I,NP
ACCUM=ZERO
DO 900 K=J,NP
ACCUM=ACCUM+DERIVS(I,K)*DERIVS(J,K)
900  CONTINUE
ACCUM=ACCUM*RESVAR
K=JPVT(I)
L=JPVT(J)
VARC(K,L)=ACCUM
VARC(L,K)=ACCUM
800  CONTINUE
700  CONTINUE
CALL DSPLAY(Y,VARC,PARAM,WK1,RESVAR,EVAL,NPTS,NP,ND1,
+ LUNOUT,JOB,IFAIL)
IF(IFAIL.NE.0)GO TO 6666
RETURN
4444  CONTINUE

```

```

WRITE(LUNOUT,30)NITS
IFAIL=1
RETURN
5555 CONTINUE
WRITE(LUNOUT,40)
IFAIL=2
RETURN
6666 CONTINUE
WRITE(LUNOUT,50)
IFAIL=8
RETURN
7777 CONTINUE
WRITE(LUNOUT,60)
IFAIL=9
RETURN
10  FORMAT(/1H ,13X,19HPARAMETER ESTIMATES
+ /1H ,10X,3HRSS,9(I13)/(1H ,13X,9(I13)))
20  FORMAT(1H ,10(E13.6)/(1H ,13X,9(E13.6)))
30  FORMAT(/1H ,38H*** SUBROUTINE SOLVE CONVERGENCE NOT,
+ 15H ACHIEVED AFTER,I10,2X,10HITERATIONS//)
40  FORMAT(/1H ,38H*** SUBROUTINE SOLVE SINGULAR MATRIX//)
50  FORMAT(/1H ,41H*** SUBROUTINE SOLVE USER-FLAGGED ERROR,
+ 19H IN SUBROUTINE EVAL//)
60  FORMAT(/1H ,45H*SUBROUTINE SOLVE RESIDUAL VARIANCE ZERA//)
END

```

```

SUBROUTINE BATES(PARAM,VAR,NITS,NPTS,NP,LUNOUT,JOB,
& EVAL,BIAS,IFAIL,A,DERIVS,RINV,QRAUX,WK1,WK2,JPVT)
C *****
C SUBROUTINE BATES CALCULATES THE BATES AND WATTS MEASURES
C OF INTRINSIC AND PARAMETER-EFFECTS CURVATURE AND BOX'S
C MEASURE OF BIAS IN THE PARAMETER ESTIMATORS
C *****
EXTERNAL EVAL
INTEGER JPVT(1),NITS,NPTS,NP,LUNOUT,JOB,IFAIL,I,J,K,NW,M,ITASK
REAL PARAM(1),A(NPTS,NP,1),DERIVS(NPTS,1),RINV(NP,1),QRAUX(1),
+ BIAS(1),WK1(1),WK2(1),VAR,STRAD,TEMP,C1,C2,W,ZERO,SQRT,FLOAT
DATA ZERO/0.0E0/
IFAIL=0
IF(VAR.LE.ZERO.OR.NP.LE.0)GO TO 2222
STRAD=SQRT(VAR*FLOAT(NP))
DO 100 I=1,NPTS
ITASK=1
CALL EVAL(PARAM,I,ITASK,WK1,IFAIL)
IF(IFAIL.NE.0)GO TO 4444
DO 200 J=1,NP
DERIVS(I,J)=WK1(J)/STRAD
200 CONTINUE
ITASK=2
CALL EVAL(PARAM,I,ITASK,WK1,IFAIL)
IF(IFAIL.NE.0)GO TO 4444
NW=0

```



```

DO 300 J=1,NP
DO 400 K=1,J
NW=NW+1
W=WK1(NW)/STRAD
A(I,J,K)=W
IF(J.NE.K)A(I,K,J)=W
400  CONTINUE
300  CONTINUE
100  CONTINUE
CALL ARRAYS(A,DERIVS,STRAD,NPTS,NP,LUNOUT,JOB)
DO 700 I=1,NP
JPVT(I)=0
700  CONTINUE
CALL SQRDC(DERIVS,NPTS,NPTS,NP,QRAUX,JPVT,WK1,1)
DO 500 I=1,NP
IF(QRAUX(I).EQ.ZERO.OR.DERIVS(I,I).EQ.ZERO)GO TO 3333
TEMP=QRAUX(I)
QRAUX(I)=DERIVS(I,I)
DERIVS(I,I)=TEMP
DO 600 J=I,NPTS
DERIVS(J,I)=-DERIVS(J,I)*QRAUX(I)
600  CONTINUE
500  CONTINUE
CALL ACCEL(A,DERIVS,RINV,QRAUX,WK1,JPVT,NPTS,NP)
CALL BOX(A,RINV,BIAS,WK1,NPTS,NP)
M=NP+1
CALL CURVE(A,DERIVS,WK1,QRAUX,WK2,C1,M,NPTS,NITS,NPTS,NP,
& IFAIL)
IF(IFAIL.EQ.0)GO TO 1111
IFAIL=5
WRITE(LUNOUT,30)NITS
1111  CONTINUE
CALL CURVE(A,DERIVS,WK1,QRAUX,WK2,C2,1,NP,NITS,NPTS,NP,IFAIL)
IF(IFAIL.EQ.6)WRITE(LUNOUT,30)NITS
CALL WATTS(A,BIAS,PARAM,C1,C2,NPTS,NP,LUNOUT,JOB)
RETURN
2222  CONTINUE
IFAIL=3
WRITE(LUNOUT,10)
RETURN
3333  CONTINUE
IFAIL=4
WRITE(LUNOUT,20)
RETURN
4444  CONTINUE
IFAIL=8
WRITE(LUNOUT,40)
RETURN
10  FORMAT(/1H ,48H*SUBROUTINE BATES INCORRECT STANDARD
& RADIUS//)
20  FORMAT(/1H ,38H*** SUBROUTINE BATES  SINGULAR MATRIX//)
30  FORMAT(/1H ,38H*** SUBROUTINE BATES  CONVERGENCE NOT,

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+ 15H ACHIEVED AFTER,I10,2X,10HITERATIONS//)
40  FORMAT(/1H ,41H*** SUBROUTINE BATES  USER-FLAGGED ERROR,
+ 19H IN SUBROUTINE EVAL//)
END

C
SUBROUTINE GNRATE(PARAM,SD,NPTS,LUNOUT,EVAL,Y,IFAIL)
C *****
C SUBROUTINE GNRATE RETURNS A VECTOR OF SIMULATED DEPENDENT
C VARIABLE VALUES WITH INDEPENDENT AND IDENTICALLY
C DISTRIBUTED NORMAL ERROR COMPONENT
C *****
EXTERNAL EVAL
INTEGER NPTS,N,I,LUNOUT,ITASK,IFAIL
REAL Y(1),PARAM(1),ERR(2),SD,W
IFAIL=0
N=0
1111 CONTINUE
CALL NORMAL(ERR)
DO 100 I=1,2
N=N+1
IF(N.GT.NPTS)GO TO 2222
ITASK=0
CALL EVAL(PARAM,N,ITASK,W,IFAIL)
IF(IFAIL.NE.0)GO TO 3333
Y(N)=W+ERR(I)*SD
100 CONTINUE
GO TO 1111
2222 CONTINUE
RETURN
3333 CONTINUE
IFAIL=8
WRITE(LUNOUT,10)
RETURN
10  FORMAT(/1H ,42H*** SUBROUTINE GNRATE  USER-FLAGGED ERROR,
+ 19H IN SUBROUTINE EVAL//)
END

C
SUBROUTINE SUMRY(STMATE,NSIM,LUNOUT,JOB,IFAIL)
C *****
C SUBROUTINE SUMARY SUPPLIES VARIOUS SUMMARY STATISTICS FOR A
C VECTOR OF PARAMETER ESTIMATES OBTAINED THROUGH SIMULATION
C *****
INTEGER NSIM,LUNOUT,JOB,MOD,I,IFAIL
REAL STMATE(1),MEAN,VAR,G1,G2
LOGICAL PRNVAL,PRNMOM,PRNFRQ
PRNVAL=JOB/100.NE.0
PRNMOM=MOD(JOB,100)/10.NE.0
PRNFRQ=MOD(JOB,10).NE.0
CALL SORT(STMATE,1,NSIM)
IF(.NOT.PRNVAL)GO TO 1111
WRITE(LUNOUT,10)(STMATE(I),I=1,NSIM)
1111 CONTINUE

```

```

      IF(NSIM.LE.1)GO TO 4444
      CALL MOMENT(STMATE,NSIM,MEAN,VAR,G1,G2)
      IF(.NOT.PRNMMOM)GO TO 2222
      WRITE(LUNOUT,20)
      WRITE(LUNOUT,30)MEAN,VAR
      WRITE(LUNOUT,40)G1,G2
2222  CONTINUE
      IF(.NOT.PRNFRQ)GO TO 3333
      CALL FREQNC(STMATE,NSIM,MEAN,VAR,LUNOUT)
3333  CONTINUE
      RETURN
4444  CONTINUE
      IFAIL=7
      WRITE(LUNOUT,50)
      RETURN
10    FORMAT(///1H ,10X,14HORDERED VALUES//(1H ,10F12.6))
20    FORMAT(///1H ,10X,23HMOMENTS OF DISTRIBUTION)
30    FORMAT(/1H ,10X,4HMEAN,17X,F20.9
+      //1H ,10X,8HVARIANCE,13X,E20.5)
40    FORMAT(/1H ,10X,20HSKEWNESS COEFFICIENT,1X,F20.9
+      //1H ,10X,15HEXCESS KURTOSIS,6X,F20.9)
50    FORMAT(/1H ,30H*** SUBROUTINE SUMRY  TOO FEW,
+      19H DEGREES OF FREEDOM//)
      END
C
      SUBROUTINE ACCEL(A,DERIVS,RINV,ALPHA,TEMPV,JPVT,NPTS,NP)
C *****
C      SUBROUTINE ACCEL TRANSFORMS THE ARRAY OF SECOND
C      DERIVATIVES TO THE ACCELERATION ARRAY USING THE RESULTS OF
C      THE QR DECOMPOSITION OF THE FIRST DERIVATIVE ARRAY
C      PERFORMED IN SUBROUTINE BATES
C *****
      INTEGER JPVT(1),NPTS,NP,I,J,K,L,IMINI,JJ,JPLUSI
      REAL A(NPTS,NP,1),DERIVS(NPTS,1),RINV(NP,1),ALPHA(1),
+      TEMPV(1),ACCUM,GAMMA,ZERO,ONE
      DATA ZERO/0.0E0/,ONE/1.0E0/
      DO 100 I=1,NP
      DO 200 J=1,I
      DO 300 K=1,NP
      ACCUM=ZERO
      DO 400 L=K,NPTS
      ACCUM=ACCUM+DERIVS(L,K)*A(L,I,J)
400    CONTINUE
      GAMMA=ACCUM/(ALPHA(K)*DERIVS(K,K))
      DO 500 L=K,NPTS
      A(L,I,J)=A(L,I,J)+GAMMA*DERIVS(L,K)
500    CONTINUE
300    CONTINUE
      DO 600 K=1,NPTS
      A(K,J,I)=A(K,I,J)
600    CONTINUE
200    CONTINUE

```

```

100  CONTINUE
      DO 700 I=1,NP
      DO 800 J=1,NP
      TEMPV(J)=ZERO
800  CONTINUE
      TEMPV(I)=ONE/ALPHA(I)
      IMIN1=I-1
      IF(IMIN1.LT.1)GO TO 1111
      DO 900 JJ=1,IMIN1
      J=IMIN1-JJ+1
      JPLUS1=J+1
      ACCUM=ZERO
      DO 1000 K=JPLUS1,NP
      ACCUM=ACCUM+DERIVS(J,K)*TEMPV(K)
1000  CONTINUE
      TEMPV(J)=-ACCUM/ALPHA(J)
900  CONTINUE
1111  CONTINUE
      DO 1100 J=1,NP
      K=JPVT(J)
      RINV(K,I)=TEMPV(J)
1100  CONTINUE
700  CONTINUE
      DO 1200 I=1,NPTS
      DO 1300 J=1,NP
      DO 1400 K=1,NP
      ACCUM=ZERO
      DO 1500 L=1,NP
      ACCUM=ACCUM+A(I,J,L)*RINV(L,K)
1500  CONTINUE
      DERIVS(J,K)=ACCUM
1400  CONTINUE
1300  CONTINUE
      DO 1600 J=1,NP
      DO 1700 K=1,J
      ACCUM=ZERO
      DO 1800 L=1,NP
      ACCUM=ACCUM+RINV(L,J)*DERIVS(L,K)
1800  CONTINUE
      A(I,J,K)=ACCUM
      A(I,K,J)=ACCUM
1700  CONTINUE
1600  CONTINUE
1200  CONTINUE
      RETURN
      END

```

C

```

SUBROUTINE ARRAYS(A,DERIVS,STRAD,NPTS,NP,LUNOUT,JOB)
C *****
C SUBROUTINE ARRAYS PRINTS THE ENTIRE FIRST DERIVATIVE MATRIX C
(DERIVS) AND THE NP FACES OF THE SECOND DERIVATIVE MATRIX (A)
C IF THESE ARE REQUIRED BY THE CURRENT CONTENTS OF JOB. THIS
C FACILITY IS INCLUDED PRIMARILY TO ALLOW THE USER TO CHECK
C THE CORRECTNESS OF THE DERIVATIVE CODING IN THE USER—
C SUPPLIED SUBROUTINE EVAL.
C *****
      INTEGER NPTS,NP,JOB,LUNOUT,I,J,K,MOD
      REAL A(NPTS,NP,1),DERIVS(NPTS,1),STRAD
      LOGICAL PRND1,PRND2
      PRND1=JOB/10000.NE.0
      PRND2=MOD(JOB,10000)/1000.NE.0
      IF((.NOT.PRND1).AND.(.NOT.PRND2))GO TO 1111
      WRITE(LUNOUT,10)STRAD
1111  CONTINUE
      IF(.NOT.PRND1)GO TO 2222
      WRITE(LUNOUT,20)
      DO 100 I=1,NPTS
      WRITE(LUNOUT,30)I,(DERIVS(I,J),J=1,NP)
100  CONTINUE
2222  CONTINUE
      IF(.NOT.PRND2)GO TO 3333
      WRITE(LUNOUT,40)
      DO 200 I=1,NP
      WRITE(LUNOUT,50)I
      DO 300 J=1,NP
      WRITE(LUNOUT,60)(A(I,J,K),K=1,NP)
300  CONTINUE
200  CONTINUE
3333  CONTINUE
      RETURN
10  FORMAT(///1H ,10X,17HSTANDARD RADIUS =,E13.6)
20  FORMAT(///1H ,10X,31HFIRST—ORDER PARTIAL DERIVATIVES,
+ 15H (STANDARDIZED)//1H ,10HDATA POINT)
30  FORMAT(1H ,I10,10X,8E12.5/(1H ,20X,8E12.5))
40  FORMAT(///1H ,10X,32HSECOND—ORDER PARTIAL DERIVATIONS,
+ 15H (STANDARDIZED)//1H ,10HDATA POINT)
50  FORMAT(1H ,I5)
60  FORMAT(1H ,10X,8E12.5/(1H ,10X,8E12.5))
      END
C
SUBROUTINE BOX(A,RINV,BIAS,TEMPV,NPTS,NP)
C *****
C SUBROUTINE BOX CALCULATES BOX'S BIAS FOR EACH PARAMETER
C ESTIMATE AND RETURNS THESE VALUES IN THE ARRAY BIAS.
C *****
      INTEGER NPTS,NP,I,J
      REAL A(NPTS,NP,1),RINV(NP,1),BIAS(1),TEMPV(1),ZERO,FLOAT
      DATA ZERO/0.0E0/
      DO 100 I=1,NP

```

```

        TEMPV(I)=ZERO
        DO 200 J=1,NP
        TEMPV(I)=TEMPV(I)+A(I,J,J)
200    CONTINUE
        TEMPV(I)=-TEMPV(I)/FLOAT(2*NP)
100    CONTINUE
        DO 300 I=1,NP
        BIAS(I)=ZERO
        DO 400 J=1,NP
        BIAS(I)=BIAS(I)+RINV(I,J)*TEMPV(J)
400    CONTINUE
300    CONTINUE
        RETURN
        END
C
        SUBROUTINE CNTEST(DIR,GRAD,COSA,SINA,THQA,NP,CNVGED)
C *****
C    SUBROUTINE CNTEST PROVIDES A CONVERGENCE TEST FOR THE
C    ITERATIVE DETERMINATION OF MAXMUM INTRINSIC OR
C    PARAMETER-EFFECTS CURVATURE.
C *****
        INTEGER NP,I
        REAL DIR(1),GRAD(1),COSA,SINA,THQA,EPS,PI,TEST,ABS,SIGN,ATAN2,
+ SGN,ZERO,ONE,TWO,PSF,SQRT
        LOGICAL CNVGED
        DATA EPS/1.0E-4/,PI/3.141592654E0/,ZERO/0.0E0/,ONE/1.0E0/,
+ TWO/2.0E0/,PSF/7.5E-1/
        CNVGED=.FALSE.
        TEST=ONE-EPS
        IF(ABS(COSA).LE.TEST)GO TO 1111
        SGN=SIGN(ONE,COSA)
        DO 100 I=1,NP
        DIR(I)=SGN*GRAD(I)
100    CONTINUE
        CNVGED=.TRUE.
        RETURN
1111    CONTINUE
        SINA=SQRT(ONE-COSA**2)
        IF(SINA.NE.ONE)GO TO 2222
        THQA=PSF*PI/TWO
        RETURN
2222    CONTINUE
        IF(COSA.GE.ZERO)GOT O 3333
        THQA=PSF*(ATAN2(SINA,COSA)+PI)
        RETURN
3333    CONTINUE
        THQA=PSF*(ATAN2(SINA,COSA))
        RETURN
        END
C

```

```

      SUBROUTINE CURVE(A,TEMPML,DIR,GRAD,TEMPL,CMAX,IM,IN,NITS,
& NPTS,NP,IFAIL)
C *****
C SUBROUTINE CURVE CALCULATES THE MAXIMUM INTRINSIC AND
C PARAMETER-EFFECT CURVATURE MEASURES BY AN ITERATIVE
C PROCEDURE WHICH TERMINATES WHEN CONVERGENCE OCCURS OR
C WHEN THE SPECIFIED MAXIMUM NUMBER OF ITERATIONS IS
C EXCEEDED. FAILURE TO CONVERGE IS FLAGGED BY THE VALUE 6 IN
C IFAIL
C *****
      INTEGER IM,IN,NITS,NPTS,NP,IFAIL,I,J,K,ITER,NPMIN1
      REAL A(NPTS,NP,1),TEMPML(NPTS,1),DIR(1),GRAD(1),TEMPL(1),
+ CMAX,ACCUM,ALENG,SINA,COSA,SIN,COS,SQRT,THQA,C1,C2,ZERO,ONE
      LOGICAL CNVGED
      DATA ZERO/0.0E0/,ONE/1.0E0/
      NPMIN1=NP-1
      IF(NPMIN1.LE.1)GO TO 1111
      DO 400 I=1,NPMIN1
      DIR(I)=ZERO
400  CONTINUE
1111  CONTINUE
      DIR(NP)=ONE
      ITER=1
2222  CONTINUE
      DO 500 I=IM,IN
      DO 600 J=1,NP
      ACCUM=ZERO
      DO 700 K=1,NP
      ACCUM=ACCUM+A(I,J,K)*DIR(K)
700  CONTINUE
      TEMPMPL(I,J)=ACCUM
600  CONTINUE
500  CONTINUE
      DO 800 I=IM,IN
      ACCUM=ZERO
      DO 900 J=1,NP
      ACCUM=ACCUM+TEMPMPL(I,J)*DIR(J)
900  CONTINUE
      TEMPL(I)=ACCUM
800  CONTINUE
      DO 1000 I=1,NP
      ACCUM=ZERO
      DO 1100 J=IM,IN
      ACCUM=ACCUM+TEMPMPL(J,I)*TEMPL(J)
1100 CONTINUE
      GRAD(I)=ACCUM
1000 CONTINUE
      ACCUM=ZERO
      DO 1200 I=1,NP
      ACCUM=ACCUM+GRAD(I)*GRAD(I)
1200 CONTINUE
      ALENG=SQRT(ACCUM)

```



```

      F(ALENG.EQ.ZERO)GO TO 4444
      DO 1300 I=1,NP
      GRAD(I)=GRAD(I)/ALENG
1300  CONTINUE
      COSA=ZERO
      DO 1400 I=1,NP
      COSA=COSA+DIR(I)*GRAD(I)
1400  CONTINUE
      CALL CNTEST(DIR,GRAD,COSA,SINA,THQA,NP,CNVGED)
      F(CNVGED)GO TO 4444
      ITER=ITER+1
      IF(ITER.LE.NITS)GO TO 3333
      IFAIL=6
      GO TO 4444
3333  CONTINUE
      C2=SIN(THQA)/SINA
      C1=COS(THQA)-C2*COSA
      DO 1500 I=1,NP
      DIR(I)=C1*DIR(I)+C2*GRAD(I)
1500  CONTINUE
      GO TO 2222
4444  CONTINUE
      DO 1600 I=IM,IN
      DO 1700 J=1,NP
      ACCUM=ZERO
      DO 1800 K=1,NP
      ACCUM=ACCUM+A(I,J,K)*DIR(K)
1800  CONTINUE
      TEMPML(I,J)=ACCUM
1700  CONTINUE
1600  CONTINUE
      DO 1900 I=IM,IN
      ACCUM=ZERO
      DO 2000 J=1,NP
      ACCUM=ACCUM+TEMPML(I,J)*DIR(J)
2000  CONTINUE
      TEMPL(I)=ACCUM
1900  CONTINUE
      ACCUM=ZERO
      DO 2100 I=IM,IN
      ACCUM=ACCUM+TEMPL(I)*TEMPL(I)
2100  CONTINUE
      CMAX=SQRT(ACCUM)
      RETURN
      END

```

C

```

      SUBROUTINE DSPLAY(Y,VARC,PARAM,WK1,VAR,EVAL,NPTS,NP,ND1,
& LUNOUT,JOB,IFAIL)
C *****
C SUBROUTINE DSPLAY PRINTS RESULTS FROM SUBROUTINE SOLVE AS
C REQUESTED BY THE SETTING OF OPTIONS SPECIFIED BY THE
C CONTENTS OF JOB.
C *****
      EXTERNAL EVAL
      INTEGER JOB,MOD,LUNOUT,ND1,NP,I,J,NPTS,IFAIL,ITASK
      REAL Y(1),VARC(ND1,1),PARAM(1),WK1(1),VAR,SQRT,T,SE,
+ YHAT,RES
      LOGICAL PRNTAB,PRNVCV,PRNCOR,PRNFIT
      PRNTAB=MOD(JOB,10000)/1000.NE.0
      PRNVCV=MOD(JOB,1000)/100.NE.0
      PRNCOR=MOD(JOB,100)/10.NE.0
      PRNFIT=MOD(JOB,10).NE.0
      IF(.NOT.PRNTAB)GO TO 1111
      WRITE(LUNOUT,10)
      DO 100 I=1,NP
      SE=SQRT(VARC(I,I))
      T=PARAM(I)/SE
      WRITE(LUNOUT,20)I,PARAM(I),SE,T
100  CONTINUE
1111 CONTINUE
      IF(.NOT.PRNVCV) GO TO 2222
      WRITE(LUNOUT,30)
      DO 200 I=1,NP
      WRITE(LUNOUT,40)I,(VARC(I,J),J=1,I)
200  CONTINUE
2222 CONTINUE
      IF(.NOT.PRNCOR)GO TO 3333
      WRITE(LUNOUT,50)
      DO 300 I=1,NP
      DO 400 J=1,I
      WK1(J)=VARC(I,J)/SQRT(VARC(I,I)*VARC(J,J))
400  CONTINUE
      WRITE(LUNOUT,60)I,(WK1(J),J=1,I)
300  CONTINUE
3333 CONTINUE
      IF(.NOT.PRNFIT)GO TO 4444
      WRITE(LUNOUT,70)
      DO 500 I=1,NPTS
      ITASK=0
      CALL EVAL(PARAM,I,ITASK,WK1,IFAIL)
      IF(IFAIL.NE.0)RETURN
      YHAT=WK1(1)
      RES=Y(I)-YHAT
      WRITE(LUNOUT,80)I,Y(I),YHAT,RES
500  CONTINUE
4444 CONTINUE
      RETURN
10  FORMAT(/1H ,10X,34HPARAMETER ESTIMATES AT CONVERGENCE/

```

```

+ /1H ,9HPARAMETER,4X,8HESTIMATE,11X,2HSE,11X,1HT)
20  FORMAT(1H ,I5, 4X,E12.6,1X,E12.6,2X,F10.2)
30  FORMAT(/1H ,10X,36HPARAMETER VARIANCE-COVARIANCE
& MATRIX//)
40  FORMAT(1H ,I5,8(2X,E12.6)/(1H ,5X,8(2X,E12.6)))
50  FORMAT(///1H ,10X,22HPARAMETER CORRELATIONS//)
60  FORMAT(1H ,I5,8(2X,F12.6)/(1H ,5X,8(2X,F12.6)))
70  FORMAT(///1H ,11X,4HUNIT,14X,1HY,9X,6HFITTED,7X,8HRESIDUAL)
80  FORMAT(1H ,I15,3E15.6)
END

```

```

C
SUBROUTINE FREQNC(X,N,MEAN,VAR,LUNOUT)
C *****
C SUBROUTINE FREQNC FORMS AND PRINTS A TABLE OF COUNTS OVER
C THE RANGE OF X-VALUES STANDARDIZED BY THE STANDARD
C DEVIATION.
C *****
C INTEGER N,LUNOUT,KOUNT,I
REAL X(1),MEAN,VAR,SD,CATINC,XX,CAT,AINT,SQRT
DATA CATINC/2.5E-1/
SD=SQRT(VAR)
KOUNT=0
XX=(X(1)-MEAN)/SD
CAT=AIN(T(XX/CATINC)*CATINC
WRITE(LUNOUT,10)
DO 100 I=1,N
XX=(X(I)-MEAN)/SD
1111 CONTINUE
IF(XX.LE.CAT)GO TO 2222
IF(KOUNT.EQ.0)GO TO 3333
WRITE(LUNOUT,20)CAT,KOUNT
KTINUE
CAT=CAT+CATINC
GO TO 1111
2222 CONTINUE
KOUNT=KOUNT+1
100 CONTINUE
WRITE(LUNOUT,20)CAT,KOUNT
RETURN
10 FORMAT(///1H ,10X,15HFREQUENCY TABLE/)
20 FORMAT(1H ,10X,F10.2,I10)
END

```

```

C
SUBROUTINE MOMENT(X,N,M1,VAR,G1,G2)
C *****
C SUBROUTINE MOMENT CALCULATES THE MEAN, VARIANCE, AND
C SKEWNESS AND EXCESS KURTOSIS COEFFICIENTS FOR THE N VALUES
C STORED IN X.
C *****
C INTEGER I,N
REAL X(1),XX,XN,M1,M2,VAR,M3,M4,G1,G2,ZERO,ONE,THREE,FLOAT,
+ SQRT

```

```

DATA ZERO/0.0E0/,ONE/1.0E0/,THREE/3.0E0/
XN=FLOAT(N)
M1=ZERO
DO 100 I=1,N
M1=M1+X(I)
100  CONTINUE
M1=M1/XN
M2=ZERO
M3=ZERO
M4=ZERO
DO 200 I=1,N
XX=X(I)-M1
M2=M2+XX**2
M3=M3+XX**3
M4=M4+XX**4
200  CONTINUE
M2=M2/XN
M3=M3/XN
M4=M4/XN
VAR=M2*XN/(XN-ONE)
G1=M3/(M2*SQRT(M2))
G2=M4/(M2**2)-THREE
RETURN
END

```

C

```

SUBROUTINE NORMAL(ERR)

```

C *****

```

C SUBROUTINE NORMAL GENERATES TWO IIDN DEVIATES FORM
C UNIFORM PSEUDO-RANDOM NUMBERS GENERATED BY THE NON-ANSI C
FORTRAN FUNCTION RNSET ON MAINFRAM MTS.

```

C *****

```

REAL ERR(2),E1,E2,E3,DEN,FAC,ZERO,ONE,TWO,RNUNF,SQRT,ALOG
DATA ZERO/0.0E0/,ONE/1.0E0/,TWO/2.0E0/
1111 CONTINUE
E1=RNUNF(0)
IF(E1.EQ.ZERO)GO TO 1111
2222 CONTINUE
E2=TWO*RNUNF(0)-ONE
E3=TWO*RNUNF(0)-ONE
DEN=E2*E2+E3*E3
IF(DEN.GT.ONE)GO TO 2222
FAC=SQRT(-TWO*ALOG(E1))
ERR(1)=FAC*(E2*E2-E3*E3)/DEN
ERR(2)=FAC*TWO*E2*E3/DEN
RETURN
END

```

C

```

SUBROUTINE SORT(A,II,JJ)
C *****
C   SUBROUTINE SORT TAKES THE PORTION OF THE REAL ARRAY A
C   BETWEEN A(II) AND A(JJ) INCLUSIVE AND SORTS IT INTO INCREASING
C   ORDER OF MAGNITUDE. ARRAYS IU(K) AND IL(K) PERMIT SORTING
C   OF UPTO 2**(K+1)-1 ELEMENTS.
C *****
      INTEGER IU(16),IL(16),I,II,J,JJ,IJ,K,M,L
      REAL A(1),T,TT
      M=1
      I=II
      J=JJ
5    IF(I.GE.J) GO TO 70
10   K=I
      IJ=(J+I)/2
      T=A(IJ)
      IF(A(I).LE.T)GO TO 20
      A(IJ)=A(I)
      A(I)=T
      T=A(IJ)
20   L=J
      IF(A(J).GE.T)GO TO 40
      A(IJ)=A(J)
      A(J)=T
      T=A(IJ)
      IF(A(I).LE.T)GO TO 40
      A(IJ)=A(I)
      A(I)=T
      T=A(IJ)
      GO TO 40
30   A(L)=A(K)
      A(K)=TT
40   L=L-1
      IF(A(L).GT.T)GO TO 40
      TT=A(L)
50   K=K+1
      IF(A(K).LT.T)GO TO 50
      IF(K.LE.L)GO TO 30
      IF(L-I.LE.J-K)GO TO 60
      IL(M)=I
      IU(M)=L
      I=K
      M=M+1
      GO TO 80
60   IL(M)=K
      IU(M)=J
      J=L
      M=M+1
      GO TO 80
70   M=M-1
      IF(M.EQ.0)RETURN
      I=IL(M)

```

```

      J=IU(M)
80  IF(J-I.GE.11)GO TO 10
      IF(I.EQ.II) GO TO 5
      I=I-1
90  I=I+1
      IF(I.EQ.J)GO TO 70
      T=A(I+1)
      IF(A(I).LE.T)GO TO 90
      K=I
100  A(K+1)=A(K)
      K=K-1
      IF(T.LT.A(K))GO TO 100
      A(K+1)=T
      GO TO 90
      END
C
      SUBROUTINE WATTS(A,BIAS,PARAM,C1,C2,NPTS,NP,LUNOUT,JOB)
C *****
C      SUBROUTINE WATTS PRINTS RESULTS FROM SUBROUTINE BATES AS
C      REQUESTED BY THE SETTING OF OPTIONS SPECIFIED BY THE
C      CONTENTS OF JOB.
C *****
      INTEGER NPTS,NP,LUNOUT,JOB,MOD,I,J,K
      REAL A(NPTS,NP,1),BIAS(1),PARAM(1),C1,C2,PERCEN,ZERO,HUNDRD
      LOGICAL PRNC,PRNB,PRNA
      DATA ZERO/0.0E0/,HUNDRD/1.0E2/
      PRNC=MOD(JOB,10).NE.0
      PRNB=MOD(JOB,100)/10.NE.0
      PRNA=MOD(JOB,1000)/100.NE.0
      IF(.NOT.PRNA)GO TO 1111
      WRITE(LUNOUT,10)
      DO 200 I=1,NP
      WRITE(LUNOUT,20)
      DO 300 J=1,NP
      WRITE(LUNOUT,30)(A(I,J,K),K=1,NP)
300  CONTINUE
200  CONTINUE
1111 CONTINUE
      IF(.NOT.PRNB)GO TO 3333
      WRITE(LUNOUT,40)
      DO 400 I=1,NP
      IF(PARAM(I).EQ.ZERO)GO TO 2222
      PERCEN=BIAS(I)/PARAM(I)*HUNDRD
      WRITE(LUNOUT,50)I,PARAM(I),BIAS(I),PERCEN
      GO TO 400
2222 CONTINUE
      WRITE(LUNOUT,50)I,PARAM(I),BIAS(I)
400  CONTINUE
3333 CONTINUE
      IF(.NOT.PRNC)GO TO 4444
      WRITE(LUNOUT,60)C1,C2
4444 CONTINUE

```



```
      RETURN
10  FORMAT(/1H ,10X,18HACCELERATION ARRAY,
+ 28H (PARAMETER-EFFECTS PORTION))
20  FORMAT(1H )
30  FORMAT(1H ,1HHX10F12.4)
40  FORMAT(/1H ,10X,10HBOX'S BIAS///1H ,8X,9HPARAMETER,9X,
+ 11HLS ESTIMATE,16X,4HBIAS,8X,12HPERCENT BIAS/)
50  FORMAT(1H ,6X,9HPARAMETER,I2,2E20.8,F20.4)
60  FORMAT(///1H ,10X,26HMAXIMUM CURVATURE MEASURES//1H ,
+ 14HINTRINSIC (IN),11X,F12.4//1H ,22HPARAMETER-EFFECTS (PE),
+ 3X,F12.4)
      END
```

EXAMPLE OF RUNNING THE PROGRAM "NONLREG.FOR"

INPUT:

PARTIAL PRESSURE AND RATE DATA

P1	P2	COS RATE
0.00242	0.02505	0.00314
0.00582	0.02078	0.00567
0.00814	0.01683	0.00887
0.01028	0.01426	0.00987
0.01130	0.01203	0.01155
0.00294	0.05516	0.00282
0.00499	0.05120	0.00618
0.00826	0.04709	0.00880
0.00900	0.04456	0.01065
0.01096	0.04329	0.01177
0.00231	0.08315	0.00321
0.00493	0.07632	0.00622
0.00815	0.07345	0.00886
0.00887	0.07003	0.01074
0.01079	0.06651	0.01187
0.00229	0.17688	0.00322
0.00487	0.17223	0.00626
0.00806	0.16849	0.00892
0.00876	0.16442	0.01081
0.01065	0.16477	0.01195

OUTPUT:

PARAMETER ESTIMATES

RSS	1	2
0.441222E-03	0.930000E-03	0.559900E+00
0.348201E-04	0.147281E-02	0.750414E+00
0.573963E-05	0.186615E-02	0.837083E+00
0.538232E-05	0.195777E-02	0.848112E+00
0.538224E-05	0.196107E-02	0.848235E+00
0.538225E-05	0.196111E-02	0.848234E+00

PARAMETER ESTIMATES AT CONVERGENCE

PARAMETER	ESTIMATE	SE	T
1	0.196111E-02	0.545643E-03	3.59
2	0.848234E+00	0.184914E-01	45.87

PARAMETER VARIANCE-COVARIANCE MATRIX

1	0.297726E-06
2	-0.733373E-05 0.341932E-03

PARAMETER CORRELATIONS

UNIT	Y	FITTED	RESIDUAL
1	1.000000		
2	-0.726853		1.000000
1	0.313600E-02	0.261591E-02	0.520087E-03
2	0.567210E-02	0.617263E-02	-0.500530E-03
3	0.887220E-02	0.843571E-02	0.436489E-03
4	0.986730E-02	0.104259E-01	-0.558626E-03

5	0.115523E-01	0.111743E-01	0.378009E-03
6	0.281850E-02	0.332387E-02	-0.505374E-03
7	0.618420E-02	0.562800E-02	0.556197E-03
8	0.879700E-02	0.928207E-02	-0.485070E-03
9	0.106540E-01	0.100913E-01	0.562701E-03
10	0.117653E-01	0.122604E-01	-0.495076E-03
11	0.320530E-02	0.265135E-02	0.553948E-03
12	0.622160E-02	0.563987E-02	0.581734E-03
13	0.886300E-02	0.931853E-02	-0.455528E-03
14	0.107378E-01	0.101209E-01	0.616916E-03
15	0.118698E-01	0.122886E-01	-0.418775E-03
16	0.322080E-02	0.266059E-02	0.560211E-03
17	0.625560E-02	0.566971E-02	0.585891E-03
18	0.891870E-02	0.937691E-02	-0.458211E-03
19	0.108059E-01	0.101819E-01	0.624035E-03
20	0.119515E-01	0.123860E-01	-0.434458E-03

ACCELERATION ARRAY (PARAMETER-EFFECTS PORTION)

-0.0688	-0.0191
-0.0191	-0.0223
-0.0191	-0.0223
-0.0223	0.0355

BOX'S BIAS

PARAMETER	LS ESTIMATE	BIAS	PERCENT BIAS
PARAMETER 1	0.196111E-02	0.978241E-05	0.4988
PARAMETER 2	0.848233E+00	0.107298E-03	0.0126

MAXIMUM CURVATURE MEASURES

INTRINSIC (IN)	0.0293
PARAMETER-EFFECTS (PE)	0.0787

PARAMETER NO. 1

MOMENTS OF DISTRIBUTION

MEAN	0.001974977
VARIANCE	0.29068E-06
SKEWNESS COEFFICIENT	0.140952229
EXCESS KURTOSIS	0.038292885

FREQUENCY TABLE

-2.50	3
-2.25	7
-2.00	9
-1.75	17
-1.50	34
-1.25	38
-1.00	58
-0.75	63
-0.50	79
-0.25	100
0.00	78
0.25	119

0.50	79
0.75	93
1.00	72
1.25	50
1.50	33
1.75	23
2.00	17
2.25	15
2.50	5
2.75	4
3.00	2
3.75	1
4.00	1

PARAMETER NO. 2
 MOMENTS OF DISTRIBUTION
 MEAN
 VARIANCE
 SKEWNESS COEFFICIENT
 EXCESS KURTOSIS

0.848200381
 0.33319E-03
 0.174372613
 -0.025636673

FREQUENCY TABLE

-3.25	1
-2.75	1
-2.50	2
-2.25	3
-2.00	9
-1.75	12
-1.50	35
-1.25	38
-1.00	50
-0.75	77
-0.50	90
-0.25	89
0.00	105
0.25	89
0.50	100
0.75	75
1.00	66
1.25	47
1.50	31
1.75	30
2.00	23
2.25	12
2.50	6
2.75	4
3.00	3
3.25	2

D.2 SIMULATION CLAUS CONVERTER PROGRAM

A Computer program "ADONEDIMBED" (developed by Minoo Razzaghi in 1985) was updated as "SMCLAUS.FOR" to evaluate the CS_2 and COS conversions in a simulated Claus converter. The program is divided into a mainline and 18 subroutines. Comments cards at the start of each routine describe its purpose. An example of input and output by running the program on the mainframe MTS is attached at the end of the program.

```

C *****
C                               MAINLINE SMCLAUS.FOR
C   THIS PROGRAM SIMULATES THE AD. ONE DIM. MODEL OF
C   CLAUS CONVERTOR
C *****
  IMPLICIT REAL*4(A-H,O-Z,$)
  EXTERNAL SNLEQ,FUN,FUNO,DF1,DF2,DF3,DF4,DF5,DF7,DF8,DF9,RATE
  #,HEATR,RFUN,SEVAL
  DIMENSION U(11),V(11),AINT(11,4),GA1(11),GA2(11),GA3(11)
  #,THIEM(11),EFF(11),TEMP(600)
  CHARACTER*1 ANS
  COMMON /GAMA/ GA1,GA2,GA3,U,V
  COMMON /COMP/ YH2S,YSO2,YH2O,YN2,DHS,DSO,DW,DS6,DENP
  COMMON /RCON/ A1,A2,A3,A4,TF0,RNF,S6F,PRESS
  COMMON /RELK/ RKH2O,RKSO2,CF0,DP
  COMMON /PARA/ S6SUR,FI,FIMOD,XS,RNS,RATES,C1,CS
  #,ZCF,ZCF0,CDIF,RKS6,POVRT
  COMMON /SURRE/TS,ETA
  DATA THIEM/.1,.2,.45,.6,.75,1.,1.5,2.,3.5,5.,8./
C*** READ IN THE INPUTS TO THE PROGRAM
  WRITE(6,100)
  WRITE(7,100)
100  FORMAT(/,5X,'INPUTS TO THE PROGRAM ARE')
C*** FEED COMPOSITION, MOLE FRACTION
  WRITE(6,*)'ENTER YH2S,YSO2,YH2O,YN2'
  WRITE(7,*)'ENTER YH2S,YSO2,YH2O,YN2'
  READ(8,*)YH2S,YSO2,YH2O,YN2
  WRITE(7,101)YH2S,YSO2,YH2O,YN2
  WRITE(6,*)'ENTER YS2,YS4,YS6,YS8'
  WRITE(7,*)'ENTER YS2,YS4,YS6,YS8'
  READ(8,*)YS2,YS4,YS6,YS8
  WRITE(7,101)YS2,YS4,YS6,YS8
C*** INLET TEMPERATURE AND PRESSURE
  WRITE(6,*)'ENTER TF0(K),PRESS(atm)'
  WRITE(7,*)'ENTER TF0(K),PRESS(atm)'
  READ(8,*)TF0,PRESS
  WRITE(7,101)TF0,PRESS
C*** BULK DIFFUSIVITIES OF H2S,SO2,H2O,S6; VISCOSITY OF THE GAS;
C*** THERMAL CONDUCTIVITY OF THE GAS.
  WRITE(6,*)'ENTER DH2SM,DSO2M,DH2OM,DS6M,VIS,TCON'
  WRITE(7,*)'ENTER DH2SM,DSO2M,DH2OM,DS6M,VIS,TCON'
  READ(8,*)DH2SM,DSO2M,DH2OM,DS6M,VIS,TCON
  WRITE(7,101)DH2SM,DSO2M,DH2OM,DS6M,VIS,TCON
C*** EFFECTIVE DIFFUSIVITIES IN THE CATALYST PELLET; H2S,
C*** SO2,H2O,S6.
  WRITE(6,*)'ENTER DHS,DSO,DW,DS6'
  WRITE(7,*)'ENTER DHS,DSO,DW,DS6'
  READ(8,*)DHS,DSO,DW,DS6
  WRITE(7,101)DHS,DSO,DW,DS6
C*** INLET SUPERSICIAL VELOCITY

```



```

WRITE(6,*)'ENTER VS0'
WRITE(7,*)'ENTER VS0'
READ(8,*)VS0
WRITE(7,101)VS0
C*** CATALYST PELLET DIAMETER, BED POROSITY, BED DENSITY,
C*** DENSITY OF THE PELLET
WRITE(6,*)'ENTER DP,EB,DENB,DENP'
WRITE(7,*)'ENTER DP,EB,DENB,DENP'
READ(8,*)DP,EB,DENB,DENP
WRITE(7,101)DP,EB,DENB,DENP
101  FORMAT(/,4X,6E15.5)
C DEFINE THE VALUES OF REACTOR PARAMETERS
CF0=YH2S*PRESS/TF0/82.06
ZCF0=2*YS2+4*YS4+6*YS6+8*YS8
ZCF0=ZCF0*PRESS/82.06/TF0
RKH2O=(DH2OM/DH2SM)**(2./3.)
RKSO2=(DSO2M/DH2SM)**(2./3.)
RKS6=(DS6M/DH2SM)**(2./3.)
CPAVE=YH2O*8.126+YN2*6.9+YH2S*7.31+YSO2*6.453
AMW=YH2O*18.+YH2S*34.+YSO2*64.+YN2*28
CPAVE=CPAVE/AMW
DEN0=AMW*PRESS/TF0/82.06
GAVE=DEN0*VS0
RE=DP*GAVE/VIS
RJD=.458/EB*(RE**(-.407))
RJH=RJD
SCH2S=(VIS/DEN0/DH2SM)**(2./3.)
CMT=RJD*GAVE/DEN0/SCH2S
PRNO=(CPAVE*VIS/TCON)**(2./3.)
CHT=RJH*CPAVE*GAVE/PRNO
C TO GET CURVE OF EFFECTIVENESS FACTOR VS MOD—THIELE
C PARAMETER, USE TF0 AS THE TEMPERATURE AT THE SURFACE. IT HAS
C BEEN SHOWN PREVIOUSLY THAT EVEN 100 DEGREE DIFFERENCE DOES
C NOT HAVE ANY EFFECT ON THE PLOT.
TS=TF0+50.
IF(YH2S.LT.0.05) TS=TF0
55  CALL EFFFAC(THIEM,EFF,TS,PRESS,HEAT)
C USE THE EFFECTIVENESS FACTOR—MOD THIELE DATA OBTAINED FOR
C INTERPOLATION BY NATURAL SPLINE METHOD.
DO 2 I=1,11
  U(I)=LOG(THIEM(I))
  V(I)=LOG(EFF(I))
2  CONTINUE
  CALL SPLN(U,V,11,AINT,GA1,GA2,GA3)
C USING THE PARAMETERS OF THE SYSTEM, DEFINE THE CONSTANTS
C OF EQUATIONS.
A1=HEAT/CPAVE*YH2S/AMW
A2=HEAT*CMT/CHT*CF0*TF0
AH=6.*(1.-EB)/DP
A3=HEAT*DENB/AH/CHT
A4=DENB/VS0/CF0
RNF=1.00

```

```

      S6F=0.1E-03
C NOW THE VARIABLES OF THE SYSTEM ARE DEFINED START
C INTGRATION
      Z0=0.0E00
      X0=0.0E00
C*** INTEGRATION STEP SIZE
      WRITE(6,*)'ENTER DELTH (cm)'
      WRITE(7,*)'ENTER DELTH (cm)'
      READ(8,*)DELTH
7   FORMAT(/,5X,'RFCON',8F15.5)
      WRITE(6,102)
      WRITE(7,102)
102  FORMAT(/,2X,'Z',10X,'XF',12X,'XS',15X,'TF',10X,'TS',12X,
# 'RATES',10X,'FIMOD',10X,'ETA',14X,'CS')
      N=1
      TEMP(N)=TF0
5   CALL RK4TH(RFUN,Z0,DELTH,X0,XF)
      Z0=Z0+DELTH
      TF=TF0+A1*XF
      WRITE(6,10)Z0,XF,XS,TF,TS,RATES,FIMOD,ETA,CS
      WRITE(7,10)Z0,XF,XS,TF,TS,RATES,FIMOD,ETA,CS
      TEMP(N+1)=TF
      N=N+1
      IF(ABS(Z0).GE.100) GO TO 20
      X0=XF
      GO TO 5
20  CONTINUE
      CALL HYDEADCS(N,DELTH,YH2O,TEMP,PRESS,ALFA)
      GO TO 46
91  CALL BALLCNDS(DP,YH2O,PRESS,ALFA)
      GO TO 47
92  CALL CYLCNDS(H,D,YH2O,PRESS,ALFA)
      GO TO 47
93  CALL HOCYCNDS(H,DO,DI,YH2O,PRESS,ALFA)
      GO TO 47
46  WRITE(6,*)'DO YOU WANT TO ESTIMATE CONCENTRATION
& DISTRIBUTION IN
& THE CATALYST PARTICLE AT A CERTAIN TEMPERATURE? (Y/N)'
      READ(5,9)ANS
9   FORMAT(A1)
94  IF(ANS.EQ.'Y'.OR.ANS.EQ.'y')THEN
      WRITE(6,*)'IS THIS A BALL CATALYST? YES OR NO (Y/N)'
      READ(5,9)ANS
      IF(ANS.EQ.'Y'.OR.ANS.EQ.'y')GOTO 91
      WRITE(6,*)'IS THIS A SOLID CYLINDRICAL CATALYST? (Y/N)'
      READ(5,9)ANS
      IF(ANS.EQ.'Y'.OR.ANS.EQ.'y')GOTO 92
      WRITE(6,*)'IS THIS A HOLLOW CYLINDRICAL CATALYST? (Y/N)'
      READ(5,9)ANS
      IF(ANS.EQ.'Y'.OR.ANS.EQ.'y')GOTO 93
      ELSE
      IF(ANS.NE.'N'.AND.ANS.NE.'n')GOTO 46

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      GOTO 11
    ENDIF
47  WRITE(6,*)'DO YOU WANT TO ESTIMATE AT ANOTHER TEMPERATURE
    & YES OR NO (Y/N)'
      READ(5,9)ANS
      GOTO 94
11  CONTINUE
10  FORMAT(F6.2,8F15.6)
      STOP
      END

```

```

C
C  SUBROUTINE HYDEADCS(N,H,CH2O,TEMP,PRESS,ALFA)
C *****
C                                SUBROUTINE "HYDEADCLS"
C  THIS SUBROUTINE ESTIMATES CS2 AND COS CONVERSION IN THE
C  ADIABATIC CLAUS CONVERTER WITH ALUMINA KAISER 201.
C  IF YOU WANT TO OBTAIN THE PERFORMANCE OF UNDEACTIVATED
C  CATALYST KAISER 201, INPUT ALFA=0.0, BETA0=1.0 AND FKK=0.0.
C  DEACTIVATION MODEL CONSIDERS UNIFORM POISONING, SHELL
C  POISONING WITH DISTRIBUTION ALONG THE BED.
C *****
C  N      =      NUMBER OF DISCRETE POINTS ALONG THE BED
C  K      =      .GE. N
C  Z(K)   =      BED AXIAL POSITION, cm
C  TIME(K) =      CONTACT TIME, s
C  TEMP(K) =      TEMPERATURE PROFILE ALONG THE BED, K
C  CS2(K)  =      CS2 CONCENTRATION ALONG THE BED, MOL%
C  COS(K)  =      COS CONCENTRATION ALONG THE BED, MOL%
C  CSK(K)  =      RATE COND TANT IN CS2 HYDROLYSIS RATE FUNCTION
C  COSK(K) =      RATE CONSTANT IN COS HYDROLYSIS RATE FUNCTION
C  CONV(K) =      CS2+COS CONVERSION, %
C  CS2KW(K) =      WATER ADSORPTION CONSTANT IN CS2 HYDROLYSIS
C                                RATE FUNCTION
C  COSKW(K) =      WATER ADSORPTION CONSTANT IN COS HYDROLYSIS
C                                RATE FUNCTION
C  EFDCS2(K) =      EFFECTIVE DIFFUSION COEFFICIENT OF CS2 MOLECULE,
C                                cm/s
C  FICS2(K) =      THIELE NUMBER OF CS2 HYDROLYSIS ON CATALYST
C  ETACS2(K) =      EFFECTIVENESS FACTOR OF CS2 HYDROLYSIS
C  EFDCOS(K) =      EFFECTIVE DIFFUSION COEFFICIENT OF COS
C                                MOLECULE, cm2/s
C  FICOS(K) =      THIELE NUMBER OF CO2 HYDROLYSIS ON CATALYST
C  ETACOS(K) =      EFFECTIVENESS FACTOR OF COS HYDROLYSIS
C  RATECS2(K)=      REACTION RATE OF CS2 HYDROLYSIS, 1/s
C  RATECOS(K)=      REACTION RATE OF COS HYDROLYSIS, 1/s
C  BETA(K)  =      UNPOISONED FRACTION OF CATALYST DIAMETER
C                                ACCORDING TO SHELL POISONED MODEL, %
C  BETA0    =      UNPOISONED FRACTION OF CATALYST DIAMETER AT
C                                TOP OF THE BED ACCORDING TO SHELL POISONING
C                                MODEL, %
C  FKK      =      PERCENTAGE OF CATALYST BED AFFECTED BY SHELL
C                                POISONING, %

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C ALFA = POISONED FRACTION OF CATALYST SURFACE ACCORDING TO
          UNIFORM POISONING MODEL, %
C Lp = CATALYST PARTICLE SIZE DEFINED BY PARTICLE VOLUME OVER
C      EXTERNAL SURFACE AREA, cm
C CH2O = WATER CONCENTRATION IN THE CONVERTER, mol%
C PRESS = PRESSURE, atm
      REAL Z(601),TIME(601),TEMP(700),CS2(601),COS(601),CS2K(601),
      $ COSK(601),CONV(601),CS2KW(601),COSKW(601),EFDCS2(601),FICS2(601),
      $ ETACS2(601),EFDCOS(601),FICOS(601),ETACOS(601),CH2O,RATECS2(601),
      $ RATECOS(601),BETA(601),Lp
      WRITE(6,*)'SATRT TO EVALUATE CONVERSION OF CS2 AND COS
      & HYDROLYSIS IN THE SIMULATION CLAUS CONVERTER'
      WRITE(7,*)'SATRT TO EVALUATE CONVERSION OF CS2 AND COS
      & HYDROLYSIS IN THE SIMULATION CLAUS CONVERTER'
      WRITE(6,*)'ENTER CHARACTERISTIC PARTICLE SIZE (Lp), UNIT cm'
      WRITE(7,*)'ENTER CHARACTERISTIC PARTICLE SIZE (Lp), UNIT cm'
      READ(5,*)Lp
      WRITE(7,*)Lp
      WRITE(6,*)'ENTER INLET CS2 AND COS CONCENTRATION, mol%'
      WRITE(7,*)'ENTER INLET CS2 AND COS CONCENTRATION, mol%'
      READ(5,*)CS2(1),COS(1)
      WRITE(7,*)CS2(1),COS(1)
      WRITE(6,*)'ENTER DEACTIVATION DEGREE: ALFA, BETA0 AND FKK, %'
      WRITE(7,*)'ENTER DEACTIVATION DEGREE: ALFA, BETA0 AND FKK, %'
      READ(6,*)ALFA,BETA0,FKK
      WRITE(7,*)ALFA,BETA0,FKK
      Z(1)=0.0
      DO 13 I=1,N
13      Z(I+1)=Z(I)+H
      DO 11 I=1,N+1
11      TIME(I)=Z(I)/100.0*3600.0/1000.0
      CONV(1)=0.0
C      START TO ESTIMATE CATALYTIC PERFORMANCE OF KAISER 201
      DO 20 I=1,N
C      ESTIMATE INTRINSIC RATE CONSTANT FOR CS2 AND COS HYDROLYSIS
      CS2K(I)=EXP(6.604-4448.0/TEMP(I))*(1.58/3600*82.05*TEMP(I))
      CS2KW(I)=EXP(-10.057+9236.00/TEMP(I))*PRESS
      AK1=(1-ALFA)*CS2K(I)*CS2KW(I)*CH2O/(1+CS2KW(I)*CH2O)
      COSK(I)=EXP(5.44-3039.0/TEMP(I))*(1.58/3600*82.05*TEMP(I))
      COSKW(I)=EXP(-11.28+1.001E4/TEMP(I))*PRESS
      AK2=(1-ALFA)*COSK(I)*COSKW(I)*CH2O/(1+COSKW(I)*CH2O)
C      ESTIMATE CATALYST EFFECTIVENESS FACTOR
      BETA(I)=1-BETA0*EXP(-6.0/FKK*(Z(I)/100))
      EFDCS2(I)=9700.0*30.0E-08*(TEMP(I)/76.13)**0.5*0.6604/4.0
      FICS2(I)=BETA(I)*Lp*(AK1/EFDCS2(I))**0.5
      ETACS2(I)=1.0/FICS2(I)*(1.0/TANH(3.0*FICS2(I))
      % -1.0/(3.0*FICS2(I)))
      ETACS2(I)=ETACS2(I)*BETA(I)**3.0/(1+(1-BETA(I))*3.0
      & *FICS2(I)**2.0*ETACS2(I))
      EFDCOS(I)=9700.0*30.0E-08*(TEMP(I)/60.27)**0.5*0.6604/4.0
      FICOS(I)=BETA(I)*Lp*(AK2/EFDCOS(I))**0.5
      ETACOS(I)=1.0/FICOS(I)*(1.0/TANH(3.0*FICOS(I))

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& -1.0/(3.0*FICOS(I)))
ETACOS(I)=ETACOS(I)*BETA(I)**3.0/(1+(1-BETA(I))*3.0
& *FICOS(I)**2.0*ETACOS(I))
20 CONTINUE
C CALCULATE THE COS CS2 EFFLUENT CONCENTRATION AND CONVERSION
DO 10 I=1,N
RATECS2(I)=ETACS2(I)*(1-ALFA)*CS2K(I)*CS2KW(I)*CH2O
& /(1+CS2KW(I)*CH2O)*CS2(I)
CS2(I+1)=CS2(I)-RATECS2(I)*(TIME(I+1)-TIME(I))
RATECOS(I)=ETACOS(I)*(1-ALFA)*COSK(I)*COSKW(I)*CH2O
& /(1+COSKW(I)*CH2O)*COS(I)
COS(I+1)=COS(I)+(RATECS2(I)-RATECOS(I))*(TIME(I+1)-TIME(I))
CONV(I+1)=CS2(1)+COS(1)-CS2(I+1)-COS(I+1)
CONV(I+1)=CONV(I+1)/(CS2(1)+COS(1))*100.00
KK=I+1
IF(CONV(I+1).GE.99.999)GOTO 66
10 CONTINUE
66 WRITE(6,*)'BALL K 201, UNIFORM PLUS SHELL POISONING ALFA=',ALFA
& ', BETA0=',BETA0,' AND FKK=',FKK
WRITE(7,*)'BALL K 201, UNIFORM PLUS SHELL POISONING ALFA=',ALFA
& ', BETA0=',BETA0,' AND FKK=',FKK
WRITE(6,*)'TIME(S) TEMP(K) CS2(MOL/ML) COS(MOL/ML) CONV% '
% ', ETACS2 ETACOS BETA'
WRITE(7,*)'TIME(S) TEMP(K) CS2(MOL/ML) COS(MOL/ML) CONV% '
% ', ETACS2 ETACOS BETA'
WRITE(6,1)(TIME(I),TEMP(I),CS2(I),COS(I),CONV(I),
& ETACS2(I),ETACOS(I),BETA(I),I=1,KK,10)
WRITE(7,1)(TIME(I),TEMP(I),CS2(I),COS(I),CONV(I),
& ETACS2(I),ETACOS(I),BETA(I),I=1,KK,10)
1 FORMAT(8F10.5)
2 FORMAT(3F10.5)
RETURN
END

SUBROUTINE BALLCNDS(D,CH2O,PRESS,ALFA)
C *****
C THIS PROGRAM ESTIMATE CS2, COS CONCENTRATION
C DISTRIBUTIONS IN THE SPHERICAL CATALYST KAISER 201
C BY CALLING SUBROUTINES BALL1 AND BALL2
C *****
REAL TEMP,CS2,COS,CS2K,COSK,CS2KW,COSKW,EFDCS2,FICS2,
$ ETACS2,EFDCOS,FICOS,ETACOS,CH2O,B(10,1),C(10),R(10)
WRITE(6,*)'START TO EVALUATE CONCENTRATION DISTRIBUTION'
WRITE(7,*)'START TO EVALUATE CONCENTRATION DISTRIBUTION'
WRITE(7,*)
WRITE(6,*)'THE CATALYST GEOMETRY IS SPHERICAL '
WRITE(7,*)'THE CATALYST GEOMETRY IS SPHERICAL '
WRITE(7,*)
WRITE(6,*)'ENTER TEMPERATURE (K) OF THE PARTICLE'
WRITE(7,*)'ENTER TEMPERATURE (K) OF THE PARTICLE'
READ(5,*)TEMP
WRITE(7,*)TEMP

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WRITE(6,*)'ENTER DIAMETER (cm) OF THE PARTICLE'
WRITE(7,*)'ENTER DIAMETER (cm) OF THE PARTICLE'
READ(5,*)D
WRITE(7,*)D
C ESTIMATE RATE CONSTANT OF CS2 AND COS HYDROLYSIS ON KAISER 201
CS2K=EXP(6.604-4448.0/TEMP)*(1.58/3600*82.05*TEMP)
CS2KW=EXP(-10.057+9236.00/TEMP)*1.5
AK1=(1-ALFA)*CS2K*CS2KW*CH2O/(1+CS2KW*CH2O)
COSK=EXP(5.44-3039.0/TEMP)*(1.58/3600*82.05*TEMP)
COSKW=EXP(-11.28+1.001E4/TEMP)*1.5
AK2=(1-ALFA)*COSK*COSKW*CH2O/(1+COSKW*CH2O)
C ESTIMATE CS2 AND COS EFFECTIVE DIFFUSIVITY
EFDOS2=9700*30.0E-08*(TEMP/76.13)**0.5*0.6604/4.0
EFDOS=9700*30.0E-08*(TEMP/60.27)**0.5*0.6604/4.0
EF1=EFDOS2
EF2=EFDOS
CS2=1.0
COS=1.0
CALL BALL1(R,D,EF1,AK1,CS2,B,C)
WRITE(6,*)'CS2 mol% DISTRIBUTION IN THE PARTICLE'
WRITE(7,*)'CS2 mol% DISTRIBUTION IN THE PARTICLE'
WRITE(6,89)(R(K),K=1,10)
WRITE(6,88)(C(K),K=1,10)
WRITE(7,89)(R(K),K=1,10)
WRITE(7,88)(C(K),K=1,10)
CALL BALL2(R,D,EF2,AK1,AK2,COS,B,C)
WRITE(6,*)'COS mol% DISTRIBUTION IN THE PARTICLE'
WRITE(7,*)'COS mol% DISTRIBUTION IN THE PARTICLE'
WRITE(6,89)(R(K),K=1,10)
WRITE(6,88)(C(K),K=1,10)
WRITE(7,89)(R(K),K=1,10)
WRITE(7,88)(C(K),K=1,10)
89  FORMAT(/,'R= ',10F7.4)
88  FORMAT(/,'C= ',10F6.3,/)
RETURN
END

SUBROUTINE BALL1(R,DI,D1,K1,K2,R(10),B(10,1),
C *****
C THIS PROGRAM IS DESIGNED TO CALCULATE CS2 CONCENTRATION
C DISTRIBUTIONS IN A SPHERICAL CATALYST
C *****
REAL AA(10,10),A(10),K1,K2,R(10),B(10,1),
& C(10),WORK(2000),D1
INTEGER I,J
NR=10
DETR=DI/2/(NR+1)
B1=DETR**2.0*K1/D1
R(1)=DETR
DO 1 I=1,NR-1
R(I+1)=R(I)+DETR
1 A(I)=DETR/R(I)

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      A(NR)=DETR/R(NR)
      DO 12 I=1,NR
      DO 12 J=1,NR
      AA(I,J)=0.0
12  CONTINUE
      DO 2 I=1,NR-1
      2  AA(I+1,I)=1-A(I+1)
      DO 3 I=1,NR
      3  AA(I,I)=-2-B1
      AA(1,1)=-1-B1-A(1)
      DO 6 I=1,NR-1
      6  AA(I,I+1)=1+A(I)
C  ENTER RIGHT HAND SIDE VALUES
      DO 61 I=1,NR
      61 B(I,1)=0.0
      B(NR,1)=-(1+A(NR))*C1O
      CALL LEQT1F(AA,1,NR,10,B,0,WORK,IER)
      DO 21 I=1,NR
      IF(B(I,1).LE.0.0)B(I,1)=0.0
      21 C(I)=B(I,1)
      RETURN
      END

```

SUBROUTINE BALL2(R,DI,D2,K1,K2,C1O,B,C)

```

C *****
C  THIS PROGRAM IS DESIGNED TO CALCULATE COS CONCENTRATION
C  DISTRIBUTIONS IN A SPHERICAL CATALYST
C *****
      REAL AA(10,10),A(10),K1,K2,R(10),B(10,1),
      & C(10),WORK(2000),D2,ETA
      INTEGER I,J
      NR=10
      DETR=DI/2/(NR+1)
      B1=DETR**2.0*K2/D2
      R(1)=DETR
      DO 1 I=1,NR-1
      R(I+1)=R(I)+DETR
1  A(I)=DETR/R(I)
      A(NR)=DETR/R(NR)
      DO 12 I=1,NR
      DO 12 J=1,NR
      AA(I,J)=0.0
12  CONTINUE
      DO 2 I=1,NR-1
      2  AA(I+1,I)=1-A(I+1)
      DO 3 I=1,NR
      3  AA(I,I)=-2-B1
      AA(1,1)=-1-B1-A(1)
      DO 6 I=1,NR-1
      6  AA(I,I+1)=1+A(I)
C  ENTER RIGHT HAND SIDE VALUES
      DO 61 I=1,NR

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```

61 B(I,1)=-B(I,1)*K1/D2*DETR**2.0
   B(NR,1)=B(NR,1)-(1+A(NR))*C1O
   CALL LEQT1F(AA,1,NR,10,B,0,WORK,IER)
   DO 21 I=1,NR
   IF(B(I,1).LE.0.0)B(I,1)=0.0
21 C(I)=B(I,1)
   RETURN
   END

C
  SUBROUTINE CYLCNDS(H,D,CH2O,PRESS,ALFA)
C *****
C   THIS PROGRAM ESTIMATE CS2 AND COS CONCENTRATION
C   DISTRIBUTIONS IN THE SOLID CYLINDRICAL CATALYST KAISER
C   201 BY CALLING SUBROUTINES CYLIND1 AND CYLIND2.
C *****
  REAL TEMP,CS2,COS,CS2K,COSK,CS2KW,COSKW,EFDOS2,FICS2,
  $ ETACS2,EFDOS,COS,FICOS,ETACOS,CH2O,B(10,1),
  & C(10,10),R(10),HT(10)
  WRITE(6,*)'START TO EVALUATE CONCENTRATION DISTRIBUTION'
  WRITE(7,*)'START TO EVALUATE CONCENTRATION DISTRIBUTION'
  WRITE(7,*)
  WRITE(6,*)'THE CATALYST GEOMETRY IS SOLID CYLINDER '
  WRITE(7,*)'THE CATALYST GEOMETRY IS SOLID CYLINDER '
  WRITE(7,*)
  WRITE(6,*)'ENTER TEMPERATURE OF THE PARTICLE'
  WRITE(7,*)'ENTER TEMPERATURE OF THE PARTICLE'
  READ(5,*)TEMP
  WRITE(7,*)TEMP
  WRITE(6,*)'ENTER HEIGHT OF THE CYLINDER (cm)'
  WRITE(7,*)'ENTER HEIGHT OF THE CYLINDER (cm)'
  READ(5,*)H
  WRITE(7,*)H
  WRITE(6,*)'ENTER DIAMETER OF THE CYLINDER (cm)'
  WRITE(7,*)'ENTER DIAMETER OF THE CYLINDER (cm)'
  READ(5,*)D
  WRITE(7,*)D
C ESTIMATE RATE CONSTANT OF CS2 AND COS HYDROLYSIS ON KAISER 201
  CS2K=EXP(6.604-4448.0/TEMP)*(1.58/3600*82.05*TEMP)
  CS2KW=EXP(-10.057+9236.00/TEMP)*1.5
  AK1=(1-ALFA)*CS2K*CS2KW*CH2O/(1+CS2KW*CH2O)
  COSK=EXP(5.44-3039.0/TEMP)*(1.58/3600*82.05*TEMP)
  COSKW=EXP(-11.28+1.001E4/TEMP)*1.5
  AK2=(1-ALFA)*COSK*COSKW*CH2O/(1+COSKW*CH2O)
C ESTIMATE C2 AND COS EFFECTIVE DIFFUSIVITY
  EFDOS2=9700*30.0E-08*(TEMP/76.13)**0.5*0.6604/4.0
  EFDOS=9700*30.0E-08*(TEMP/60.27)**0.5*0.6604/4.0
  EF1=EFDOS2
  EF2=EFDOS
  CS2=1.0
  COS=1.0
  CALL CYLIND1(HT,R,D,H,EF1,AK1,CS2,B,C)
  WRITE(6,*)'CS2 mol% DISTRIBUTION'

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WRITE(7,*)'CS2 mol% DISTRIBUTION'
WRITE(6,89)(R(K),K=1,10)
WRITE(7,89)(R(K),K=1,10)
DO 9 J=1,10
WRITE(6,88)HT(J),(C(K,J), K=1,10)
9 WRITE(7,88)HT(J),(C(K,J), K=1,10)
CALL CYLIND2(HT,R,D,H,EF2,AK1,AK2,COS,B,C)
WRITE(6,*)'COS mol% DISTRIBUTION'
WRITE(7,*)'COS mol% DISTRIBUTION'
WRITE(6,89)(R(K),K=1,10)
WRITE(7,89)(R(K),K=1,10)
DO 19 J=1,10
WRITE(6,88)HT(J),(C(K,J), K=1,10)
19 WRITE(7,88)HT(J),(C(K,J), K=1,10)
89 FORMAT(/,'R= ',20F7.4)
88 FORMAT(/,'H= ',11F6.3)
RETURN
END

```

```

SUBROUTINE CYLIND1(HT,R,DI,H,D1,K1,C1O,B,C)
C *****
C THIS PROGRAM IS DESIGNED TO CALCULATE CS2 CONCENTRATION
C DISTRIBUTIONS IN A SOLID CYLINDRICAL CATALYST
C *****
REAL AA(100,100),A(10),D1,K1,R(10),B(100,1),HT(10),G(10),
&C(10,10),WORK(10000)
INTEGER I,J
NR=10
NZ=10
DETR=H/2/(NR+1)
DETZ=DI/2/(NZ+1)
B1=(DETR/DETZ)**2.0
HT(1)=DETZ
DO 11 I=1,NZ-1
11 HT(I+1)=HT(I)+DETZ
R(1)=DETR
DO 1 I=1,NR-1
R(I+1)=R(I)+DETR
A(I)=1-DETR/R(I)/2
1 G(I)=1+DETR/R(I)/2
A(NR)=1-DETR/R(NR)/2
G(NR)=1+DETR/R(NR)/2
D=-2-2*B1-DETR**2.0*K1/D1
DO 12 I=1,NR*NZ
DO 12 J=1,NR*NZ
AA(I,J)=0.0
12 CONTINUE
DO 2 J=1,NZ*NR,NR
K=1
DO 2 I=J,NR+J-2
AA(I+1,I)=A(K+1)
2 K=K+1

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      DO 3 J=1,NR*NZ,NR
      DO 3 I=J,NR+J-1
3    AA(I,I)=D
      DO 4 I=1,NR
4    AA(I,I)=B1+D
      AA(1,1)=B1+D+A(1)
      DO 5 J=1,NZ-1
5    AA(J*NR+1,J*NR+1)=A(1)+D
      DO 6 J=1,NR*NZ,NR
      K=1
      DO 6 I=J,NR+J-2
      AA(I,I+1)=G(K)
6    K=K+1
      DO 41 J=1,NZ*(NR-1),NR
      DO 41 I=J,NR+J-1
      AA(I,I+NR)=B1
41   AA(I+NR,I)=B1
C   ENTER RIGHT HAND SIDE VALUES
      DO 61 I=1,NR*NZ
61   B(I,1)=0.0
      DO 7 J=1,NZ
7    B(J*NR,1)=-G(NR)*C1O
      B(NR*NZ,1)=-(G(NR)+B1)*C1O
      DO 8 I=1,NR-1
8    B(NZ*NR-NR+I,1)=-B1*C1O
      CALL LEQT1F(AA,1,NR*NZ,100,B,0,WORK,IER)
      K=1
      DO 22 J=1,NZ
      DO 21 I=1,NR
      IF(B(K-1+I,1).LE.0.0)B(K-1+I,1)=0.0
21   C(I,J)=B(K-1+I,1)
22   K=K+NR
      RETURN
      END

```

```

      SUBROUTINE CYLIND2(HT,R,DI,H,D2,K1,K2,C1O,B,C)
C *****
C   THIS PROGRAM IS DESIGNED TO CALCULATE COS CONCENTRATION
C   DISTRIBUTIONS IN A SOLID CYLINDRICAL CATALYST
C *****
      REAL AA(100,100),A(10),K1,K2,R(10),B(100,1),HT(10),G(10),
      &C(10,10),WORK(10000),CC
      INTEGER I,J
      NR=10
      NZ=10
      DETR=H/2/(NR+1)
      DETZ=DI/2/(NZ+1)
      B1=(DETR/DETZ)**2.0
      HT(1)=DETZ
      DO 11 I=1,NZ-1
11   HT(I+1)=HT(I)+DETZ
      R(1)=DETR

```

```

DO 1 I=1,NR-1
R(I+1)=R(I)+DETR
A(I)=1-DETR/R(I)/2
1 G(I)=1+DETR/R(I)/2
A(NR)=1-DETR/R(NR)/2
G(NR)=1+DETR/R(NR)/2
D=-2-2*B1-DETR**2.0*K2/D2
DO 12 I=1,NR*NZ
DO 12 J=1,NR*NZ
AA(I,J)=0.0
12 CONTINUE
DO 2 J=1,NZ*NR,NR
K=1
DO 2 I=J,NR+J-2
AA(I+1,I)=A(K+1)
2 K=K+1
DO 3 J=1,NR*NZ,NR
DO 3 I=J,NR+J-1
3 AA(I,I)=D
DO 4 I=1,NR
4 AA(I,I)=B1+D
AA(1,1)=B1+D+A(1)
DO 5 J=1,NZ-1
5 AA(J*NR+1,J*NR+1)=A(1)+D
DO 6 J=1,NR*NZ,NR
K=1
DO 6 I=J,NR+J-2
AA(I,I+1)=G(K)
6 K=K+1
DO 41 J=1,NZ*(NR-1),NR
DO 41 I=J,NR+J-1
AA(I,I+NR)=B1
41 AA(I+NR,I)=B1
C ENTER RIGHT HAND SIDE VALUES
DO 61 I=1,NR*NZ
61 B(I,1)=B(I,1)*K1/D2*DETR**2.0
DO 7 J=1,NZ
7 B(J*NR,1)=-G(NR)*C1O-B(J*NR,1)
B(NR*NZ,1)=-(G(NR)+B1)*C1O-B(NR*NZ,1)
DO 8 I=1,NR-1
8 B(NZ*NR-NR+I,1)=-B1*C1O-B(NZ*NR-NR+I,1)
CALL LEQTF(AA,1,NR*NZ,100,B,0,WORK,IER)
K=1
DO 22 J=1,NZ
DO 21 I=1,NR
IF(B(K-1+I,1).LE.0.0)B(K-1+I,1)=0.0
21 C(I,J)=B(K-1+I,1)
22 K=K+NR
RETURN
END

```

```

SUBROUTINE HOCYCND(S,H,DO,DI,CH2O,PRESS,ALFA)
C *****
C THIS PROGRAM ESTIMATE CS2 AND COS CONCENTRATION
C DISTRIBUTIONS IN THE HOLLOW CYLINDRICAL CATALYST KAISER 201
C BY CALLING SUBROUTINES CYLHOLL1 AND CYLHOLL2
C *****
    REAL CS2,COS,CS2K,COSK,CS2KW,COSKW,EFDOS2,
$ B(100,1),C(10,10),R(10),HT(10),CH2O,TEMP,PRESS
    WRITE(6,*)'START TO EVALUATE CONCENTRATION DISTRIBUTION'
    WRITE(7,*)'START TO EVALUATE CONCENTRATION DISTRIBUTION'
    WRITE(7,*)
    WRITE(6,*)'THE CATALYST GEOMETRY IS HOLLOW CYLINDER '
    WRITE(7,*)'THE CATALYST GEOMETRY IS HOLLOW CYLINDER '
    WRITE(7,*)
    WRITE(6,*)'ENTER TEMPERATURE OF THE PARTICLE'
    WRITE(7,*)'ENTER TEMPERATURE OF THE PARTICLE'
    READ(5,*)TEMP
    WRITE(7,*)TEMP
    WRITE(6,*)'ENTER HEIGHT OF THE HOLLOW CYLINDER'
    WRITE(7,*)'ENTER HEIGHT OF THE HOLLOW CYLINDER'
    READ(6,*)H
    WRITE(7,*)H
    WRITE(6,*)'ENTER OUTSIDE DIAMETER OF THE HOLLOW CYLINDER'
    WRITE(7,*)'ENTER OUTSIDE DIAMETER OF THE HOLLOW CYLINDER'
    READ(6,*)DO
    WRITE(7,*)DO
    WRITE(6,*)'ENTER THE HOLLOW DIAMETER OF THE HOLLOW
CYLINDER'
    WRITE(7,*)'ENTER THE HOLLOW DIAMETER OF THE HOLLOW
CYLINDER'
    READ(6,*)DI
    WRITE(7,*)DI
C ESTIMATE RATE CONSTANT FOR CS2 AND COS HYDROLYSIS
    CS2K=EXP(6.604-4448.0/TEMP)*(1.58/3600*82.05*TEMP)
    CS2KW=EXP(-10.057+9236.00/TEMP)*PRESS
    AK1=(1-ALFA)*CS2K*CS2KW*CH2O/(1+CS2KW*CH2O)
    COSK=EXP(5.44-3039.0/TEMP)*(1.58/3600*82.05*TEMP)
    COSKW=EXP(-11.28+1.001E4/TEMP)*PRESS
    AK2=(1-ALFA)*COSK*COSKW*CH2O/(1+COSKW*CH2O)
C ESTIMATE CS2 AND COS EFFECTIVE DIFFUSIVITY
    EFDOS2=9700*30.0E-08*(TEMP/76.13)**0.5*0.6604/4.0
    EFDOS=9700*30.0E-08*(TEMP/60.27)**0.5*0.6604/4.0
    EF1=EFDOS2
    EF2=EFDOS
    CS2=1.0
    COS=1.0
    CALL CYLHOLL1(HT,R,DO,DI,H,EF1,AK1,CS2,B,C)
    WRITE(6,*)'CS2 mol% DISTRIBUTION '
    WRITE(7,*)'CS2 mol% DISTRIBUTION '
    WRITE(6,89)(R(K),K=1,10)
    WRITE(7,89)(R(K),K=1,10)
    DO 9 J=1,10

```



```

      WRITE(6,88)HT(J),(C(K,J), K=1,10)
9    WRITE(7,88)HT(J),(C(K,J), K=1,10)
      CALL CYLHOLL2(HT,R,DO,DI,H,EF2,AK1,AK2,COS,B,C)
      WRITE(6,*)'COS mol% DISTRIBUTION '
      WRITE(7,*)'COS mol% DISTRIBUTION '
      WRITE(6,89)(R(K),K=1,10)
      WRITE(7,89)(R(K),K=1,10)
      DO 19 J=1,10
      WRITE(6,88)HT(J),(C(K,J), K=1,10)
19   WRITE(7,88)HT(J),(C(K,J), K=1,10)
89   FORMAT(/,'r= ',20F7.4)
88   FORMAT(/,'H= ',11F6.3)
      RETURN
      END

```

```

      SUBROUTINE CYLHOLL1(HT,R,DO,DI,H,D1,K1,C1O,B,C)

```

```

C *****
C THIS PROGRAM IS DESIGNED TO CALCULATE CS2 CONCENTRATION
C DISTRIBUTIONS IN A HOLLOW CYLINDRICAL CATALYST
C *****
      REAL AA(100,100),A(10),K1,R(10),B(100,1),HT(10),G(10),
      &C(10,10),WORK(10000),D1
      INTEGER I,J
      NR=10
      NZ=10
      DETR=(DO-DI)/2/(NR+1)
      DETZ=H/2/(NZ+1)
      B1=(DETR/DETZ)**2.0
      HT(1)=DETZ
      DO 11 I=1,NZ-1
11   HT(I+1)=HT(I)+DETZ
      R(1)=DETR+DI/2.0
      DO 1 I=1,NR-1
      R(I+1)=R(I)+DETR
      A(I)=1-DETR/R(I)/2.0
1   G(I)=1+DETR/R(I)/2.0
      A(NR)=1-DETR/R(NR)/2.0
      G(NR)=1+DETR/R(NR)/2.0
      D=-2.0-2.0*B1-DETR**2.0*K1/D1
      DO 12 I=1,NR*NZ
      DO 12 J=1,NR*NZ
      AA(I,J)=0.0
12  CONTINUE
      DO 2 J=1,NZ*NR,NR
      K=1
      DO 2 I=J,NR+J-2
      AA(I+1,I)=A(K+1)
2   K=K+1
      DO 3 J=1,NR*NZ,NR
      DO 3 I=J,NR+J-1
3   AA(I,I)=D
      DO 4 I=1,NR

```

```

4  AA(I,I)=B1+D
   DO 5 J=1,NZ-1
5  AA(J*NR+1,J*NR+1)=D
   DO 6 J=1,NR*NZ,NR
   K=1
   DO 6 I=J,NR+J-2
   AA(I,I+1)=G(K)
6  K=K+1
   DO 41 J=1,NZ*(NR-1),NR
   DO 41 I=J,NR+J-1
   AA(I,I+NR)=B1
41  AA(I+NR,I)=B1
C  ENTER RIGHT HAND SIDE VALUES
   DO 61 I=1,NR*NZ
61  B(I,1)=0.0
   DO 7 J=1,NZ
7  B(J*NR,1)=-G(NR)*C10
   B(NR*NZ,1)=-G(NR)+B1)*C10
   DO 8 I=1,NR-1
8  B(NZ*NR-NR+I,1)=-B1*C10
   KKK=1
   DO 9 J=1,NZ
   B((KKK-1)+1,1)=B((KKK-1)+1,1)-A(1)*C10
9  KKK=NZ+KKK
   CALL LEQTF(AA,1,NR*NZ,100,B,0,WORK,IER)
   K=1
   DO 22 J=1,NZ
   DO 21 I=1,NR
   IF(B(K-1+I,1).LE.0.0)B(K-1+I,1)=0.0
21  C(I,J)=B(K-1+I,1)
22  K=K+NR
C  CALCULATE EFFICIENCY
   RETURN
   END

SUBROUTINE CYLHOLL2(HT,R,DO,DI,H,D2,K1,K2,C10,B,C)
C *****
C  THIS SUBROUTINE IS DESIGNED TO CALCULATE COS CONCENTRATION
C  DISTRIBUTIONS IN A HOLLOW CYLINDRICAL CATALYST
C *****
   REAL AA(100,100),A(10),K1,K2,R(10),B(100,1),HT(10),G(10),
&  C(10,10),WORK(10000),D2
   INTEGER I,J
   NR=10
   NZ=10
   DETR=(DO-DI)/2.0/(NR+1)
   DETZ=H/2.0/(NZ+1)
   B1=(DETR/DETZ)**2.0
   HT(1)=DETZ
   DO 11 I=1,NZ-1
11  HT(I+1)=HT(I)+DETZ
   R(1)=DETR+DI/2.0

```

```

DO 1 I=1,NR-1
R(I+1)=R(I)+DETR
A(I)=1-DETR/R(I)/2.0
1 G(I)=1+DETR/R(I)/2.0
A(NR)=1-DETR/R(NR)/2.0
G(NR)=1+DETR/R(NR)/2.0
D=-2.0-2.0*B1-DETR**2.0*K2/D2
DO 12 I=1,NR*NZ
DO 12 J=1,NR*NZ
AA(I,J)=0.0
12 CONTINUE
DO 2 J=1,NZ*NR,NR
K=1
DO 2 I=J,NR+J-2
AA(I+1,I)=A(K+1)
2 K=K+1
DO 3 J=1,NR*NZ,NR
DO 3 I=J,NR+J-1
3 AA(I,I)=D
DO 4 I=1,NR
4 AA(I,I)=B1+D
DO 5 J=1,NZ-1
5 AA(J*NR+1,J*NR+1)=D
DO 6 J=1,NR*NZ,NR
K=1
DO 6 I=J,NR+J-2
AA(I,I+1)=G(K)
6 K=K+1
DO 41 J=1,NZ*(NR-1),NR
DO 41 I=J,NR+J-1
AA(I,I+NR)=B1
41 AA(I+NR,I)=B1
C ENTER RIGHT HAND SIDE VALUES
DO 61 I=1,NR*NZ
61 B(I,1)=B(I,1)*K1/D2*DETR**2.0
DO 7 J=1,NZ
7 B(J*NR,1)=-G(NR)*C1O-B(J*NR,1)
B(NR*NZ,1)=-(G(NR)+B1)*C1O-B(NR*NZ,1)
DO 8 I=1,NR-1
8 B(NZ*NR-NR+I,1)=-B1*C1O-B(NZ*NR-NR+I,1)
KKK=1
DO 9 J=1,NZ
B((KKK-1)+1,1)=B((KKK-1)+1,1)-A(1)*C1O-B((KKK-1)+1,1)
9 KKK=NZ+KKK
CALL LEQT1F(AA,1,NR*NZ,100,B,0,WORK,IER)
K=1
DO 22 J=1,NZ
DO 21 I=1,NR
IF(B(K-1+I,1).LE.0.0)B(K-1+I,1)=0.0
21 C(I,J)=B(K-1+I,1)
22 K=K+NR
RETURN

```

```

      END
C *****
C FOR DETAILED DESCRIPTIONS FOR THE FOLLOWING SUBROUTINES,
C REFER TO DR. MINOO RAZZAGHI'S THESIS, "MODELLING OF THE
C CATALYTIC CLAUS PROCESS", APRIL, 1985, UNIV. OF ALBERTA
C *****
      SUBROUTINE RK4TH(FCN,T0,H,X0,X)
C THIS SUBROUTINE ADVANCES THE SOLUTION OF A FIRST ORDER
C DIFFERENTIAL EQUATION OF THE FORM DX/DT=F(X,T), USING THE
C RUNGE-KUTTA 4TH ORDER METHOD.
C PARAMETERS ARE:
C FCN FUNCTION SUBPROGRAM TO COMPUTE DX/DT=F(X,T)
C THIS FUNCTION MUST BE DECLARED EXTERNAL BY THE CALLING
C PROGRAM
C X0 & T0 VALUES OF X & T AT THE BEGINING OF THE INTERVAL
C H STEP SIZE
C X VALUE AT THE END OF INTERVAL
      IMPLICIT REAL*4(A-H,O-Z,$)
      XK1=H*FCN(X0,T0)
      XK2=H*FCN(X0+XK1/2.,T0+H/2.)
      XK3=H*FCN(X0+XK2/2.,T0+H/2.)
      XK4=H*FCN(X0+XK3,T0+H)
      X=X0+(XK1+2.*XK2+2.*XK3+XK4)/6.
      RETURN
      END
C
      FUNCTION RFUN(XF,Z)
      IMPLICIT REAL*4(A-H,O-Z,$)
      DIMENSION PAR(13),DF(12,12),Y(2)
      COMMON/COMP/YH2S,YO2,YH2O,YN2,DHS,DSO,DW,DS6,DENP
      COMMON/PARA/S6SUR,FI,FIMOD,XS,RNS,RATES,C1,CS
      #,ZCF,ZCF0,CDIF,RKS6,POVRT
      COMMON/RFCN/A1,A2,A3,A4,TF0,RNF,S6F,PRESS
      COMMON/SURRES/TS,ETA
      TF=TF0+A1*XF
      IF(XF.LT.0.9E-06) GO TO 1
      NCALL=1
      ICALL=1
      NEQ=2
C CALL SNLEQ TO GET S6 , TOTAL MOLES CORRESPONDING TO THE FLUID
C CONDITION. FIRST GET THE EQUILIBRIUM CONSTANTS AT THE FLUID
C CONDITION.
      CALL EQCTS(TF,PRESS,PAR)
      PAR(4)=YH2S*XF
      PAR(6)=YO2
      PAR(7)=YH2O
      PAR(11)=YH2S
      PAR(12)=YN2
      Y(1)=S6F
      Y(2)=RNF
C NOW CALCULATE TOTAL MOLES TO GET FLUID CONCENTRATION.
      CALL SNLEQ(RHS,TF,PRESS,Y,PAR,1.E00,1,2,ICALL,NI,YH2S,DF,NEQ)

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      S6F=Y(1)
      RNF=Y(2)
C NOW DEFINE THE PARAMETERS REQUIRED FOR GETTING TS & XS
1  U=PRESS/RNF/82.06/TF
    POVRT=U*RNF
    CFH2O=(YH2O+YH2S*XF)*U
    CFSO2=(YSO2-.5*YH2S*XF)*U
    ZCF=ZCF0+6./4.*YH2S*POVRT*XF
    TS1=TF+1.E00
    TS2=TF+3.0E00
    CALL TEMS(TS1,TS2,TF,XF,CFH2O,CFSO2)
C NOW DEFINE THE DIFFERENTIAL
    RFUN=RATES*ETA*A4
    RETURN
    END
C
    SUBROUTINE EQCTS(T,PRESS,PAR)
C THIS SUBROUTINE EVALUTES THE EQUILIBRIUM CONSTANTS. PLEASE
C NOTE DIFFERENT EQUATIONS FOR K USING THE PUBLISHED AND
C ADJUSTED FREE ENERGY DATA.
    IMPLICIT REAL*4(A-H,O-Z,$)
    DIMENSION PAR(13)
    RLK62=-34173./T+37.9735
C DISTORTED FREE ENERGY DATA
    RLK64=-13663.9/T+12.6028
    RLK68=2932./T-3.43174
    RLK=11050.1/T-11.5576
    RK=EXP(RLK)
    RK62=EXP(RLK62)
    RK64=EXP(RLK64)
    RK68=EXP(RLK68)
    AA=(RK62/PRESS/PRESS)**(1./3.)
    BB=(RK64/SQRT(PRESS))**(2./3.)
    CC=(RK68*(PRESS** 25))**(4./3.)
    PAR(1)=AA
    PAR(2)=BB
    PAR(3)=CC
    PAR(5)=RK
    PAR(8)=PAR(5)*SQRT(PRESS)
    RETURN
    END
C
    SUBROUTINE TEMS(TS1,TS2,TF,XF,CFH2O,CFSO2)
    IMPLICIT REAL*4(A-H,O-Z,$)
    DIMENSION F(100),T(100),GA1(11),GA2(11),GA3(11),X(3),U(11),
    $V(11),PAR(13),DF(12,12)
    COMMON/GAMA/GA1,GA2,GA3,U,V
    COMMON/COMP/YH2S,YSO2,YH2O,YN2,DHS,DSO,DW,DS6,DENP
    COMMON/RELK/RKH2O,RKSO2,CF0,DP
    COMMON/RFCON/A1,A2,A3,A4,TF0,RNF,S6F,PRESS
    COMMON/PARA/S6SUR,FI,FIMOD,XS,RNS,RATES,C1,CS
    #,ZCF,ZCF0,CDIF,RKS6,POVRT

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```

COMMON/SURRES/TS,ETA
COMMON/CALL/NCALL,NTYPE
PAR(6)=YH2S
PAR(7)=YH2O
PAR(9)=DHS/DW
PAR(10)=DHS/DSO
PAR(11)=YH2S
PAR(12)=YN2
PAR(13)=DHS/DS6
NCALL=0
NEQ=2
I=1
TS=TS1
5  XS=1.+TS/A2*(TS-TF)-TS/TF*(1.-XF)
   CDIF=CF0*TF0*((1.-XS)/TS-(1.-XF)/TF)
   CSH2O=CFH2O-RKH2O*CDIF
   CSSO2=CFSO2+.5*RKSO2*CDIF
   PSH2O=CSH2O*82.06*TS
   PSSO2=CSSO2*82.06*TS
   CALL EQCTS(TS,PRESS,PAR)
   X(1)=S6F
   X(2)=RNF
   PAR(4)=YH2S*XS
   CALL SNLEQ(RHS,TS,PRESS,X,PAR,.5E00,1,2,1,NI,YH2S,DF,NEQ)
   S6SUR=X(1)
   RNS=X(2)
18  NTYPE=2
   RATES=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,XS,S6SUR,RNS)
C   IF(I.GT.1) GO TO 10
   CS=CF0*(1.-XS)*TF0/TS
C IF RATES IS NEGATIVE, THE ASSUMED TS IS TOO LARGE ,REDUCE IT
   IF(RATES) 40,45,45
40  TS=TF
   GO TO 5
45  FI=DP/6.*SQRT(ABS(RATES/CS*DENP/DHS))
   X(1)=0.006
   X(2)=1.0
   X(3)=0.75
C LET NCALL BE 2 TO GET CONDITION INSIDE THE PELLET.
   NCALL=2
   NEQ=3
   CALL SNLEQ(RHS,TS,PRESS,X,PAR,1.E00,1,3,2,NI,YH2S,DF,NEQ)
C RESET NCALL TO 1 AND NEQ TO 2 BECAUSE FROM NOW ON
C ONLY SURFACE CONDITION IS CONSIDERED AT THIS VALUE
C OF XF & TF .
   NCALL=0
   NEQ=2
   XEQ=X(3)
   RNE=X(2)
   C1=(1.-XEQ)/(1.-XS)*RNS/RNE
   FIMOD=FI/SQRT(ABS(1.-C1))
   IF(FIMOD.LT..9E-01) GO TO 25

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FIM=LOG(FIMOD)
ETA=SEVAL(11,FIM,U,V,GA1,GA2,GA3)
ETA=EXP(ETA)
GO TO 10
25  ETA=1.E00
10  F(I)=TS-TF-A3*RATES*ETA
    T(I)=TS
    IF(I-2) 12,13,20
12  TS=TS2
    I=I+1
    GO TO 5
13  IF(ABS(T(2)-T(1)).GT..1E-10) GO TO 20
    TS=TF+.01
    I=2
    GO TO 5
20  DIFF=(F(I)-F(I-1))/(T(I)-T(I-1))
    TSC=TS-.75*F(I)/DIFF
    IF(ABS(TSC-TS).LT.1.E-02) GO TO 30
    TS=TSC
    I=I+1
    GO TO 5
30  TS=TSC
    RETURN
    END
C
FUNCTION HEATR(V1,V2,V3,V4,TS)
IMPLICIT REAL*4(A-H,O-Z,$)
DH298=-35008.8+V1*31200+V2*34810+V3*24360+V4*24320
DCP=-4.818121+V1*8.54+V2*19.092+V3*31.58+V4*42.67
HEATR=DH298+DCP*(TS-298)
HEATR=-HEATR
C THIS IS HEAT FOR 2 MOLES OF REACTED H2S. TO GET
C HEAT PER MOLE OF H2S DIVIDE BY 2.
HEATR=HEATR/2.
RETURN
END
C
SUBROUTINE SNLEQ(RHS,TS,PRESS,X,PAR,W,M,N,ICALL,NI,YH2S,DF,NEQ)
C THIS SUBROUTINE SOLVES SYSTEM OF NONLINEAR
C EQ'S BY NEWTON'S METHOD.
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION FSAVE(12),X(12),F(12,1),DF(NEQ,NEQ),WKAREA(1000)
&,Z(5),XSAVE(12),PAR(13),Y(2)
500 FORMAT(5F14.5)
IA=NEQ
IDGT=0
MAXIT=200
FTOL=.1E-4
XTOL=.1E-4
NUM=N+1
IF(NEQ.EQ.N) NUM=N
DO 100 I=1,MAXIT

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      DO 110 J=1,NUM
110  XSAVE(J)=X(J)
330  FORMAT(/,6F15.6)
C   ICALL=1 FOR SURFACE , ICALL=2 FOR EQUILIBRIUM , AND
C   ICALL=3 FOR PROFILE ESTIMATION.
      IF(ICALL.EQ.1) GO TO 70
      IF(ICALL.EQ.2) GO TO 75
C   ICALL=5 TO GET N,S6,X FOR GIVEN SI
      IF(ICALL.EQ.5) GO TO 900
      DO 30 II=1,NEQ
      DO 30 J=1,NEQ
30   DF(J,II)=0.0
      KK=1
      DO 10 KI=1,N,3
      F(KI,1)=FUNO(TS,PRESS,NI,N,KK,PAR)
      DF(KI,KI)=DF1(TS,PRESS,NI,KK,PAR)
      DF(KI,KI+1)=DF5(TS,PRESS,NI,KK,PAR)
      DF(KI,KI+2)=DF3(TS,PRESS,NI,KK,PAR)
      KK=KK+1
10   CONTINUE
      DO 20 KI=2,N,3
      PAR(4)=X(KI-1)
      Y(1)=X(KI)
      Y(2)=X(KI+1)
      F(KI,1)=FUN(Y,1,PAR)
      DF(KI,KI-1)=DF9(Y,1,PAR)
      F(KI+1,1)=FUN(Y,2,PAR)
      DF(KI,KI)=DF7(Y,1,PAR)
      DF(KI,KI+1)=DF8(Y,1,PAR)
      DF(KI+1,KI-1)=DF9(Y,2,PAR)
      DF(KI+1,KI)=DF7(Y,2,PAR)
      DF(KI+1,KI+1)=DF8(Y,2,PAR)
20   CONTINUE
21   IF (NI.EQ.1) GO TO 58
      KK=1
      DO 60 KI=1,N,3
      KKK=1
      DO 50 KJ=1,N,3
      IF(KI.EQ.KJ) GO TO 55
      DF(KI,KJ)=DF2(NI,KK,KKK)
      DF(KI,KJ+2)=DF4(KK,KKK,NI)
55   KKK=KKK+1
50   CONTINUE
      KK=KK+1
60   CONTINUE
58   CONTINUE
      GO TO 80
70   F(1,1)=FUN(X,1,PAR)
      F(2,1)=FUN(X,2,PAR)
      DF(1,1)=DF7(X,1,PAR)
      DF(1,2)=DF8(X,1,PAR)
      DF(2,1)=DF7(X,2,PAR)

```

```

      DF(2,2)=DF8(X,2,PAR)
2000  FORMAT(/,30F15.6)
3500  FORMAT(/,30F15.6)
      GO TO 80
75   PAR(4)=X(3)
      F(1,1) = FUN(X,1,PAR)
      F(2,1) = FUN(X,2,PAR)
      F(3,1) = FUN(X,3,PAR)
      DF(1,1) = DF7(X,1,PAR)
      DF(1,2) = DF8(X,1,PAR)
      DF(1,3) = DF9(X,1,PAR)
      DF(2,1) = DF7(X,2,PAR)
      DF(2,2) = DF8(X,2,PAR)
      DF(2,3) = DF9(X,2,PAR)
      DF(3,1) = DF7(X,3,PAR)
      DF(3,2) = DF8(X,3,PAR)
      DF(3,3)=DF9(X,3,PAR)
      GO TO 80
900  PAR(4)=X(3)
      F(1,1)=FUN(X,1,PAR)
      F(2,1)=FUN(X,2,PAR)
      F(3,1)=RHS-(1.E00-X(3))/X(2)
      DF(1,1)=DF7(X,1,PAR)
      DF(1,2)=DF8(X,1,PAR)
      DF(1,3)=DF9(X,1,PAR)
      DF(2,1)=DF7(X,2,PAR)
      DF(2,2)=DF8(X,2,PAR)
      DF(2,3)=DF9(X,2,PAR)
      DF(3,1)=0.0E00
      DF(3,2)=(1.E00-X(3))/X(2)/X(2)
      DF(3,3)=1.E00/X(2)
80   ITEST=0
C SCALING THE JACOBIAN MATRIX
      DO 92 ISS=1,NEQ
      SCALE=ABS(DF(ISS,1))
      DO 90 IS=1,NEQ
      IF(ABS(DF(ISS,IS)).GT.SCALE) SCALE=ABS(DF(ISS,IS))
90   CONTINUE
      DO 91 IS=1,NEQ
      DF(ISS,IS)=DF(ISS,IS)/SCALE
91   CONTINUE
      F(ISS,1)=F(ISS,1)/SCALE
92   CONTINUE
      DO 220 J=1,NEQ
      FSAVE(J)=F(J,1)
      F(J,1)=-F(J,1)
220  CONTINUE
33   CALL LEQT1F(DF,M,NEQ,IA,F,IDGT,WKAREA,IER)
      DO 1000 II=1,NEQ
      X(II)=XSAVE(II)+W*F(II,1)
1000 CONTINUE
1001 DO 550 JJ=1,NEQ

```

```

      IF(ABS(F(JJ,1)).GT.XTOL) ITEST=ITEST+1
      IF(FSAVE(JJ).GT.FTOL) ITEST=ITEST+1
550  CONTINUE
C  IF TOL MET PRINT THE RESULT
      IF(ITEST.EQ.0) GO TO 200
100  CONTINUE
      WRITE(6,400)
      WRITE(7,400)
400  FORMAT(//,'CONVERGENCE WAS NOT ACHIEVED AFTER 100 ITER.')
      RETURN
200  CONTINUE
350  RETURN
      END
C
      FUNCTION FUN(X,K,PAR)
      IMPLICIT REAL*4(A-H,O-Z,$)
      DIMENSION X(3),PAR(13)
      COMMON /VAR/ P1,P2,P3,P4,P5,P6,P7,P8,P9,PPH2O,PPH2S,PPSO2
      #,ZW,ZWS
      COMMON /PAR/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
      #,ZCF,ZCF0,CDIF,RKS6,POVRT
      COMMON/CALL/NCALL,NTYPE
      P1=(X(1)*X(2)*X(2))**(1./3.)
      P2=(X(1)*X(1)*X(2))**(1./3.)
      P3=((X(1)**4)/X(2))**(1./3.)
      P4=(X(2)/X(1))**(2./3.)
      P5=SQRT(P4)
      P6=(X(1)/X(2))**(1./3.)
      P7=P3/X(2)
      IF(NCALL.LT.2) GO TO 30
      P8=(PAR(7)+PAR(11)*XS)/RNS
      P9=(PAR(6)-PAR(11)*XS/2.)/RNS
      A=(1.-XS)/RNS-(1.-PAR(4))/X(2)
      P10=P8+PAR(9)*PAR(11)*A
      PPSO2=P9-PAR(10)*PAR(11)*A/2.
      ZWS=(S6SUR/RNS)**(1./3.)
      ZW=(X(1)/X(2))**(1./3.)
      ZSOVP=2.*PAR(1)*ZWS+4.*PAR(2)*ZWS*ZWS+6.*S6SUR/RNS+
      #8.*PAR(3)*ZWS**4
      ZOVP=2.*PAR(1)*ZW+4.*PAR(2)*ZW*ZW+6.*X(1)/X(2)+
      #8.*PAR(3)*ZW**4
      GO TO (6,11,20),K
6    FUN=X(2)*(PPH2O+PPSO2-1.)+PAR(11)*(1.-PAR(4))
      #+PAR(1)*P1+PAR(2)*P2+X(1)+PAR(3)*P3+PAR(12)
      RETURN
11   FUN=ZOVP-ZSOVP-6./4.*PAR(13)*PAR(11)*A
      RETURN
20   PPH2S=PAR(11)*(1.-X(3))/X(2)
      FUN=PAR(8)*(PPH2S**2)*(PPSO2)
      FUN=FUN-(PPH2O**2)*SQRT(ABS(X(1)/X(2)))
      RETURN
30   GO TO (5,10),K

```

```

5   FUN=1.-.5*PAR(4)+PAR(1)*P1+PAR(2)*P2+X(1)+PAR(3)*P3-X(2)
    RETURN
10  IF(NCALL.EQ.0) GO TO 12
    FUN=2.*PAR(1)*P1+4.*PAR(2)*P2+6.*X(1)+8.*PAR(3)*P3-1.5*PAR(4)
    RETURN
12  ZCS=POVRT*(2.*PAR(1)*P1+4.*PAR(2)*P2+6.*X(1)+8.*PAR(3)*P3)
    FUN=ZCS-ZCF+6./4.*RKS6*CDIF
    RETURN
    END

```

C

```

    FUNCTION DF7(X,K,PAR)
    IMPLICIT REAL*4(A-H,O-Z,$)
    DIMENSION X(3),PAR(13)
    COMMON /VAR/ P1,P2,P3,P4,P5,P6,P7,P8,P9,PPH2O,PPH2S,PPSO2
    #,ZW,ZWS
    COMMON /PAR/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
    #,ZCF,ZCF0,CDIF,RKS6,POVRT
    COMMON/CALL/NCALL,NTYPE
    GO TO (5,10,20) , K
5   DF7=PAR(1)*P4/3.+2.*PAR(2)*P5/3.+1.+4./3.*PAR(3)*P6
    RETURN
10  IF(NCALL.EQ.0) GO TO 11
    DF7=2./3.*PAR(1)/P2+8./3.*PAR(2)/P1+6./X(2)+32./3.*PAR(3)*P6/X(2)
    RETURN
11  DF7=POVRT*(2./3.*PAR(1)*P4+8./3.*PAR(2)/P6+6.+32./3.*PAR(3)*P6)
    RETURN
20  DF7=-0.5E00*(PPH2O**2)/SQRT(ABS(X(1)*X(2)))
    RETURN
    END

```

C

```

    FUNCTION DF8(X,K,PAR)
    IMPLICIT REAL*4(A-H,O-Z,$)
    DIMENSION X(3),PAR(13)
    COMMON /VAR/ P1,P2,P3,P4,P5,P6,P7,P8,P9,PPH2O,PPH2S,PPSO2
    #,ZW,ZWS
    COMMON /PAR/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
    #,ZCF,ZCF0,CDIF,RKS6,POVRT
    COMMON/CALL/NCALL,NTYPE
    IF(NCALL.GT.1) GO TO 50
    GO TO (5,10) , K
5   DF8=2./3.*PAR(1)/P5+PAR(2)/3./P4-PAR(3)*P7/3.-1.
    RETURN
10  DF8=4./3.*PAR(1)/P5+4./3.*PAR(2)/P4-8.*PAR(3)*P7/3.
    IF(NCALL.EQ.0) DF8=DF8*POVRT
    RETURN
50  GO TO (60,70,80) ,K
60  DF8=2./3.*PAR(1)*P6+1./3.*PAR(2)/P4-1./3.*PAR(3)*P7-1.
    DF8=DF8+PPH2O+PPSO2+(PAR(9)-PAR(10)/2.)*PAR(11)
    #*(1.-PAR(4))/X(2)
    RETURN
70  DF8=-2./3.*PAR(1)*P6/X(2)-8./3.*PAR(2)/P4/X(2)-6.*X(1)/X(2)/X(2)
    #-32./3.*PAR(3)*P3/X(2)/X(2)-6./4.*PAR(13)*PAR(11)*(1.-PAR(4))

```

```

# /X(2)/X(2)
RETURN
80  DPH2O=PAR(9)*PAR(11)*(1.-X(3))/(X(2)**2)
    DPSO2=-PAR(10)*PAR(11)*(1.-X(3))/(X(2)**2)
    DPH2S=-PAR(11)*(1.-X(3))/(X(2)**2)
    DF8=2.*PAR(8)*PPH2S*PPSO2*DPH2S
    DF8=DF8+PAR(8)*(PPH2S**2)*DPSO2
    DF8=DF8-2.*PPH2O*DPH2O*SQRT(ABS(X(1)/X(2)))
    DF8=DF8+.5*(PPH2O**2)*SQRT(ABS(X(1)))*(X(2)**(-1.5))
    RETURN
END

C
  FUNCTION DF9(X,K,PAR)
C THIS FUNCTION CALCULATES THE DIFFERENTIAL WITH RESPECT TO
C CONVERSION.
    IMPLICIT REAL*4(A-H,O-Z,$)
    DIMENSION X(3),PAR(13)
    COMMON /VAR/P1,P2,P3,P4,P5,P6,P7,P8,P9,PPH2O,PPH2S,PPSO2
    #,ZW,ZWS
    COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
    #,ZCF,ZCF0,CDIF,RKS6,POVRT
    COMMON/CALL/NCALL,NTYPE
    GO TO (5,10,20),K
5    DF9=PAR(11)*(PAR(9)-.5*PAR(10)-1.0)
    RETURN
10   DF9=-6./4.*PAR(13)*PAR(11)/X(2)
    RETURN
20   DPH2O=PAR(9)*PAR(11)/X(2)
    DPSO2=-PAR(10)*PAR(11)/2./X(2)
    DPH2S=-PAR(11)/X(2)
    DF9=2.*PAR(8)*PPH2S*PPSO2*DPH2S
    DF9=DF9+PAR(8)*(PPH2S**2)*DPSO2
    DF9=DF9-2.*PPH2O*DPH2O*SQRT(ABS(X(1)/X(2)))
    RETURN
END

C
  FUNCTION FUNO(TS,PRESS,NI,N,J,PAR)
    IMPLICIT REAL*4(A-H,O-Z,$)
    DIMENSION X(12),B(5,5),B1(5,5),Z(5),A(5,5),PAR(13),
    #QINV(5,5)
    COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
    #,ZCF,ZCF0,CDIF,RKS6,POVRT
    COMMON /ORTH/ B,B1,A,X,QINV,Z
    COMMON/CALL/NCALL,NTYPE
    FUNO=0.0
    K=1
    DO 10 I=1,N,3
5    FUNO=FUNO+B(J,K)*((1.-X(I))/(1.-XS)*RNS/X(I+2)
    #-C1)/(1.E00-C1)
30   K=K+1
10   CONTINUE
    M=J+2*(J-1)

```



```

R=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,X(M),X(M+1),X(M+2))
40 FUNO=FUNO+B(J,NI+1)-9.*FIMOD*FIMOD*R/RATES
60 RETURN
END
C
FUNCTION DF1(TS,PRESS,NI,J,PAR)
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION X(12),B(5,5),B1(5,5),Z(5),A(5,5),PAR(13)
#,QINV(5,5)
COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
#,ZCF,ZCF0,CDIF,RKS6,POVRT
COMMON /ORTH/ B,B1,A,X,QINV,Z
COMMON/CALL/NCALL,NTYPE
K=J+2*(J-1)
5 DF1=-B(J,J)/(1.-XS)*RNS/X(K+2)/(1.E00-C1)
20 R1=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,X(K),X(K+1),X(K+2))
CONV=X(K)+0.00001
R2=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,CONV,X(K+1),X(K+2))
DR=(R2-R1)/.00001
30 DF1=DF1-9.*FIMOD*FIMOD*DR/RATES
50 RETURN
END
C
FUNCTION DF2(NI,J,I)
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION X(12),B(5,5),B1(5,5),Z(5),A(5,5),PAR(13)
#,QINV(5,5)
COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
#,ZCF,ZCF0,CDIF,RKS6,POVRT
COMMON /ORTH/ B,B1,A,X,QINV,Z
K=I+2*(I-1)
5 DF2=-B(J,I)*RNS/(1.-XS)/X(K+2)/(1.E00-C1)
20 RETURN
END
C
FUNCTION DF3(TS,PRESS,NI,J,PAR)
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION X(12),B(5,5),B1(5,5),Z(5),A(5,5),PAR(13)
#,QINV(5,5)
COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
#,ZCF,ZCF0,CDIF,RKS6,POVRT
COMMON /ORTH/ B,B1,A,X,QINV,Z
COMMON/CALL/NCALL,NTYPE
K=J+2*(J-1)
5 DF3=-B(J,J)*(1.-X(K))/(1.-XS)*RNS/(X(K+2)**2)/(1.E00-C1)
20 R1=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,X(K),X(K+1),X(K+2))
CM=X(K+2)+.00001
R2=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,X(K),X(K+1),CM)
DR=(R2-R1)/.00001
30 DF3=DF3-9.*FIMOD*FIMOD/RATES*DR
50 RETURN
END

```

```

FUNCTION DF4(J,I,NI)
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION X(12),B(5,5),B1(5,5),Z(5),A(5,5),PAR(13)
#,QINV(5,5)
COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
#,ZCF,ZCF0,CDIF,RKS6,POVRT
COMMON /ORTH/ B,B1,A,X,QINV,Z
M=I+2*(I-1)
5  DF4=-B(J,I)*(1.-X(M))/(1.-XS)*RNS/(X(M+2)**2)/(1.E00-C1)
20 RETURN
END

C
FUNCTION DF5(TS,PRESS,NI,J,PAR)
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION X(12),B(5,5),B1(5,5),Z(5),A(5,5),PAR(13)
#,QINV(5,5)
COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
#,ZCF,ZCF0,CDIF,RKS6,POVRT
COMMON /ORTH/ B,B1,A,X,QINV,Z
COMMON/CALL/NCALL,NTYPE
K=J+2*(J-1)
R1=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,X(K),X(K+1),X(K+2))
CS6=X(K+1)+.00001
R2=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,X(K),CS6,X(K+2))
DR=(R2-R1)/.00001
10 DF5=-9.*FIMOD*FIMOD*DR/RATES
20 RETURN
END

C
FUNCTION RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,Z1,S6,TM)
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION PAR(13)
COMMON /COMP/ YH2S,YSO2,YH2O,YN2,DHS,DSO,DW,DS6,DENP
COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
#,ZCF,ZCF0,CDIF,RKS6,POVRT
EQK=PAR(5)/SQRT(760.E00)
IF(NTYPE.EQ.2) GO TO 10
PSO2=(YSO2-YH2S*XS/2.)/RNS-YH2S*DHS/DSO/2.
#*((1.-XS)/RNS-(1.-Z1)/TM)
PSO2=PSO2*PRESS*760.
PH2O=(YH2O+YH2S*XS)/RNS+YH2S*DHS/DW
#*((1.-XS)/RNS-(1.-Z1)/TM)
PH2O=PH2O*PRESS*760.
GO TO 20
10 PSO2=PSSO2*760.
PH2O=PSH2O*760.
20 PH2S=YH2S*(1.-Z1)/TM*PRESS*760.
PS6=S6/TM*760.*PRESS
COEF=1.0
AB=COEF*2.56E-04*EXP(-7350./1.986/TS)
RATE=AB/((1.+0.006E00*PH2O)**2)
RATE=RATE*(PH2S*SQRT(PSO2)-PH2O*SQRT(SQRT(PS6)/ABS(EQK)))

```

```

      RETURN
      END
C
      SUBROUTINE SOLYI(YI,RKISI,AYI,NFLAG)
      IMPLICIT REAL*4(A-H,O-Z,$)
      DIMENSION XX(3)
      PI=3.141592654E00
      B=(3.*RKISI-2.)/(1.-RKISI)
      C=(6.*RKISI+AYI-2.-3.*AYI*RKISI)/AYI/(1.-RKISI)
      DE=RKISI*(AYI-6.)/AYI/(1.-RKISI)
      P=C-B*B/3.
      Q=(2.*(B**3)-9.*B*C+27.*DE)/27.
      D=(P/3.)**3+(Q/2.)**2
70    FORMAT(/,'CUBIC',2(3F19.9))
      IF(D) 10,10,40
10    E=ABS(P)
      F=-Q/2./SQRT(ABS((E**3)/27.))
      ANGLE=ARCOS(F)
      E=ABS(E)
      Y1=2.*SQRT(E/3.)*COS(ANGLE/3.)
      Y2=-2.*SQRT(E/3.)*COS((ANGLE+PI)/3.)
      Y3=-2.*SQRT(E/3.)*COS((ANGLE-PI)/3.)
      XX(1)=Y1-B/3.
      D=ABS(D)
      XX(2)=Y2-B/3.
      XX(3)=Y3-B/3.
      YI=0.0E00
      DO 15 I=1,3
      IF(XX(I).GE.0.0E00.AND.XX(I).LE.(1.0E00)) YI=XX(I)
15    CONTINUE
      IF(YI.GE.0.0E00) GO TO 30
      WRITE(6,1) (XX(I),I=1,3)
      WRITE(7,1) (XX(I),I=1,3)
1    FORMAT(/,5X,'NO SOLUTION FOR YI IN 0-1 RANGE ',3F16.8)
      NFLAG=-1
      WRITE(7,1) (XX(I),I=1,3)
      RETURN
30    WRITE(6,2) YI
2    FORMAT(/,'REACTION INTERPHASE:',F15.8)
      NFLAG=1
      RETURN
40    U=-Q/2.+SQRT(D)
      U=U**(1./3.)
      V=-Q/2.-SQRT(D)
      V=V**(1./3.)
      Y1=V+U
      XX(1)=Y1-B/3.
      IF(XX(1).GE.0.0E00.AND.XX(1).LE.1.E00) GO TO 50
      NFLAG=-1
      RETURN
50    YI=XX(1)
      NFLAG=1

```

```

WRITE(6,2) YI
RETURN
END

SUBROUTINE SPLN(X,Y,N,A,B,C,D)
IMPLICIT REAL*4(A-H,O-Z,$)
DIMENSION X(N),Y(N),A(N,4),B(N),C(N),D(N)
C THIS SUBROUTINE COMPUTES THE MATRIX FOR FINDING THE
C COEFFICIENTS OF A NATURAL CUBIC SPLINE THROUGH A
C SET OF DATA.
C PARAMETERS ARE:
C X,Y          ARRAYS OF X&Y TO BE FITTED
C              X IN STRICTLY INCREASING ORDER
C S            ARRAYS OF SECOND DERIVATIVES
C N            NUMBER OF POINTS
C A            AUGMENTED MATRIX OF COEFFICIENTS AND R.H.S
C B,C,D        ARRAYS OF POLYNOMIAL COEFFICIENTS
IF(N.LT.3) GO TO 50
C COMPUTE FOR THE N-2 ROWS
NM2=N-2
NM1=N-1
DX1=X(2)-X(1)
D(1)=DX1
DY1=(Y(2)-Y(1))/DX1*6.
DO 10 I=1,NM2
DX2=X(I+2)-X(I+1)
D(I+1)=DX2
DY2=(Y(I+2)-Y(I+1))/DX2*6.
A(I,1)=DX1
A(I,2)=2.*(DX1+DX2)
A(I,3)=DX2
A(I,4)=DY2-DY1
DX1=DX2
DY1=DY2
10 CONTINUE
C NOW SOLVE THE TRIANGULAR SYSTEM, FIRST REDUCE.
DO 20 I=2,NM2
A(I,2)=A(I,2)-A(I,1)/A(I-1,2)*A(I-1,3)
A(I,4)=A(I,4)-A(I,1)/A(I-1,2)*A(I-1,4)
20 CONTINUE
C NOW BACK SUBSTITUE
A(NM2,4)=A(NM2,4)/A(NM2,2)
DO 30 I=2,NM2
J=NM1-I
A(J,4)=(A(J,4)-A(J,3)*A(J+1,4))/A(J,2)
30 CONTINUE
C NOW PUT THE VAULES IN TO SIGMA VECTOR OF FORSYTHE ETAL TEXT
C WHICH IS S VECTOR/6 HERE C VECTOR IS SIGMA VECTOR
DO 40 I=1,NM2
C(I+1)=A(I,4)/6.
40 CONTINUE
C SIGMA(1)=SIGMA(N)=0. FOR NATURAL SPLINE

```

```

      C(1)=0.0E00
      C(N)=0.0E00
C  NOW COMPUTE POLYNOMINAL COEFFICIENTS
      B(N) = (Y(N) - Y(NM1))/D(NM1) + D(NM1)*(C(NM1) + 2.*C(N))
      DO 540 I = 1, NM1
      B(I) = (Y(I+1) - Y(I))/D(I) - D(I)*(C(I+1) + 2.*C(I))
      D(I) = (C(I+1) - C(I))/D(I)
      C(I) = 3.*C(I)
540  CONTINUE
      C(N) = 3.*C(N)
      D(N) = D(N-1)
      RETURN
50  B(1) = (Y(2)-Y(1))/(X(2)-X(1))
      C(1) = 0.
      D(1) = 0.
      B(2) = B(1)
      C(2) = 0.
      D(2) = 0.
      RETURN
      END

C
      FUNCTION SEVAL(N,U,X,Y,B,C,D)
      IMPLICIT REAL*4(A-H,O-Z,$)
      DIMENSION X(N),Y(N),B(N),C(N),D(N)
      DATA I/1/
      IF ( I .GE. N ) I = 1
      IF ( U .LT. X(I) ) GO TO 410
      IF ( U .LE. X(I+1) ) GO TO 430
410  I = 1
      J = N+1
420  K = (I+J)/2
      IF ( U .LT. X (K) ) J = K
      IF ( U .GE. X (K) ) I = K
      IF ( J .GT. I + 1 ) GO TO 420
430  DX=X(I)-X(I)
      SEVAL = Y(I)+DX*(B(I)+DX*(C(I)+DX*D(I)))
      DERIV=B(I)+DX*(2.0*C(I)+DX*(3.0*D(I)))
      RETURN
      END

C
      SUBROUTINE EFFFAC(THIEM,EFF,TS,PRESS,HEAT)
      IMPLICIT REAL*4 (A-H,O-Z,$)
      DIMENSION X(12),DF(12,12),B(5,5),B1(5,5),A40(2,2),
      * B40(2,2),B140(2,2),Z40(2),QINV40(2,2),
      * A41(3,3),B41(3,3),B141(3,3),Z41(3),QINV41(3,3),
      * A42(4,4),B42(4,4),B142(4,4),Z42(4),QINV42(4,4),
      * A43(5,5),B43(5,5),B143(5,5),Z43(5),QINV43(5,5),
      * THIEM(11),EFF(11),Y(3),Z(5),QINV(5,5),A(5,5),PAR(13)
      COMMON /COMP/ YH2S,YSO2,YH2O,YN2,DHS,DSO,DW,DS6,DENP
      COMMON /PARA/ S6SUR, FI,FIMOD,XS,RNS,RATES,C1,CS
      #,ZCF,ZCF0,CDIF,RKS6,POVRT
      COMMON /ORTH/ B,B1,A,X,QINV,Z

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COMMON /CALL/NCALL,NTYPE
DATA A40/-0.387298E+01,0.387298E+01,-0.500000E+01,0.500000E+01/
DATA B40/-0.150000E+02,0.150000E+02,-0.150000E+02,0.150000E+02/
DATA B140/-0.500000E+01,0.500000E+01,-0.500000E+01,0.500000E+01/
DATA Z40/0.7745966692E+00,0.1000000000E+01/
DATA QINV40/0.250000E+01,-0.150000E+01,-0.250000E+01,0.250000E+01/
DATA A41/-0.3544027272E+01,0.8049184963E+01,-0.4505157690E+01,
% -0.8593033528E+00,-0.6722341582E+01,0.7581644935E+01,
& 0.9482702063E+00,-0.1494827061E+02,0.1400000040E+02/
DATA B41/-0.1359530870E+02,0.2042831058E+02,-0.6833001879E+01,
% 0.1457168997E+02,-0.9140469478E+02,0.7683300481E+02,
% 0.2405439203E+02,-0.1290543955E+03,0.1050000035E+03/
DATA B141/-0.4319688219E+00,-0.9468230637E+01,0.9900199459E+01,
& 0.1646823038E+02,-0.7656803385E+02,0.6009980347E+02,
& 0.2215785162E+02,-0.9915785430E+02,0.7700000268E+02/
DATA Z41/0.5384693101E+00,0.9061798495E+00,0.100000E+01/
DATA QINV41/0.2177062574E+01,-0.3052062656E+01,0.1875000082E+01,
& -0.4828260250E+01,0.1357826062E+02,-0.8750000367E+01,
& 0.2651197677E+01,-0.1052619796E+02,0.7875000284E+01/
DATA A42/-0.418186E+01,0.820264E+01,-0.101910E+02,0.617023E+01,
& -0.989277E+00,-0.367021E+01,0.100343E+02,-0.537484E+01,
& 0.279030E+00,-0.227802E+01,-0.111486E+02,0.131476E+02,
% -0.377090E+00,0.272361E+01,-0.293465E+02,0.270000E+02/
DATA B42/-0.200257E+02,0.266019E+02,-0.125721E+02,0.599590E+01,
& 0.108779E+02,-0.449190E+02,0.517498E+02,-0.177087E+02,
& -0.677872E+01,0.682366E+02,-0.313055E+03,0.251597E+03,
% -0.196883E+02,0.131043E+03,-0.489355E+03,0.378000E+03/
DATA B142/0.582448E+00,-0.138206E+02,0.376490E+02,-0.244109E+02,
& 0.135461E+02,-0.350200E+02,0.246860E+02,-0.321205E+01,
& -0.736671E+01,0.730370E+02,-0.289562E+03,0.223892E+03,
& -0.189342E+02,0.125596E+03,-0.430662E+03,0.324000E+03/
DATA Z42/0.4058451514E+00,0.7415311856E+00,0.9491079123E+00,
& 0.1000000000E+01/
DATA QINV42/0.209160E+01,-0.243862E+01,0.353451E+01,-0.218750E+01,
& -0.821736E+01,0.199513E+02,-0.314214E+02,0.196875E+02,
& 0.103484E+02,-0.339485E+02,0.669125E+02,-0.433125E+02,
& -0.422269E+01,0.164358E+02,-0.390256E+02,0.268125E+02/
DATA A43/-0.498836E+01,0.936546E+01,-0.951917E+01,0.133917E+02,
& -0.824963E+01,-0.115593E+01,-0.342882E+01,0.846320E+01,-0.959694E+01,
& 0.571849E+01,0.323055E+00,-0.232707E+01,-0.457122E+01,0.138289E+02,
& -0.725362E+01,-0.135396E+00,0.786144E+00,-0.411984E+01,-0.169989E+02,
$ 0.204680E+02,0.196336E+00,-0.110267E+01,0.508680E+01,-0.481805E+02,
$ 0.440000E+02/
DATA B43/&-0.293168E+02,0.380222E+02,-0.138935E+02,0.111666E+02,
$ -0.597852E+01,0.127352E+02,-0.485888E+02,0.476969E+02,-0.230895E+02,
$ 0.112462E+02,-0.361360E+01,0.376383E+02,-0.110325E+03,0.117187E+03,
% -0.402871E+02,0.481371E+01,-0.297170E+02,0.194228E+03,-0.801769E+03,
% 0.632445E+03,0.169890E+02,-0.932721E+02,0.395312E+03,-0.130903E+04,
% 0.990000E+03/
DATA B143/0.145148E+01,-0.197440E+02,0.448209E+02,-0.714336E+02,
& 0.449053E+02,0.165043E+02,-0.374086E+02,0.201012E+02,0.820298E+01,
& -0.739987E+01,-0.438643E+01,0.426053E+02,-0.993894E+02,0.841052E+02,

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& -0.229346E+02,0.509340E+01,-0.313410E+02,0.202738E+03,-0.766653E+03,
& 0.590163E+03,0.165963E+02,-0.910667E+02,0.385138E+03,-0.121267E+04,
& 0.902000E+03/
DATA Z43/0.3242534234E+00,0.6133714327E+00,0.8360311073E+00,
& 0.9681602395E+00,0.1000000000E+01/
DATA QINV43/0.205616E+01,-0.224956E+01,0.269595E+01,-0.396349E+01,
& 0.246094E+01,-0.126568E+02,0.292638E+02,-0.383794E+02,0.578661E+02,
& -0.360937E+02,%0.273890E+02,-0.838855E+02,0.138839E+03,-0.223108E+03,
& 0.140766E+03,-0.251303E+02,0.895293E+02,-0.175866E+03,0.312561E+03,
& -0.201094E+03,0.834200E+01,-0.326580E+02,0.727111E+02,-0.143356E+03,
& 0.949609E+02/
XS=.5E00
IF(YH2S.LT.0.05) XS=0.1E00
CALL EQCTS(TS,PRESS,PAR)
PAR(4)=YH2S*XS
PAR(6)=YSO2
PAR(7)=YH2O
PAR(9)=DHS/DW
PAR(10)=DHS/DSO
PAR(11)=YH2S
PAR(12)=YN2
PAR(13)=DHS/DS6
NCALL=1
X(1)=.02
X(2)=.98
NEQ=2
CALL SNLEQ(RHS,TS,PRESS,X,PAR,1.E00,1,2,1,NI,YH2S,DF,NEQ)
S6SUR=X(1)
RNS=X(2)
NTYPE=1
RATES=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,XS,S6SUR,RNS)
C EVALUATE STIOCHIMETRIC COEFFICIENTS FOR THIS AVERAGE
C CONVERSION AND FEED TEMPERATURE. ASSUME THIS IS CONSTANT
C THROUGH THE BED WITH REGARD TO HEAT OF REACTION
C CALCULATION.
S2=PAR(1)*(S6SUR*RNS*RNS)**(1./3.)
S4=PAR(2)*(S6SUR*S6SUR*RNS)**(1./3.)
S8=PAR(3)*((S6SUR**4)/RNS)**(1./3.)
C REACTION: 2H2S+SO2=2H2O+V1 S2+V2 S4+V3 S6+V4 S8
V1=2.*S2/YH2S/XS
V2=2.*S4/YH2S/XS
V3=2.*S6SUR/YH2S/XS
V4=2.*S8/YH2S/XS
HEAT=HEATR(V1,V2,V3,V4,TS)
C..... NOW SNLEQ IS USED TO GET EQUILIBRIUM CONVERSION .....
C..... HERE X(1) IS S6EQ, X(2) MOLE AT EQ, AND X(3) EQCONV .....
C..... NOW ICALL=2 & NCALL=2 .....
NEQ=3
NCALL=2
WRITE(6,1)
1 FORMAT('ESTIMATE OF S6,N AND XEQ AT THE CENTER OF THE PELLET ')
WRITE(6,*)'ENTER X(1), X(2), X(3)'

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WRITE(7,*)'ENTER X(1), X(2), X(3)'
READ(8,*)X(1),X(2),X(3)
WRITE(7,*)X(1), X(2), X(3)
CALL SNLEQ(RHS,TS,PRESS,X,PAR,.5E00,1,3,2,NI,YH2S,DF,NEQ)
S6EQ=X(1)
RNE=X(2)
XEQ=X(3)
C C1 IS CEQ./C AT THE SURFACE
C1=(1.-XEQ)/(1.-XS)*RNS/RNE
DO 2000 II=1,11
FIMOD=THIEM(II)
FI=FIMOD*(SQRT(ABS(1.-C1)))
IF(II.EQ.1) NI=1
IF(II.EQ.2) NI=2
IF(II.EQ.3) GO TO 1109
IF(II.EQ.4) NI=3
IF(II.EQ.5.OR.II.EQ.6) GO TO 1109
IF(II.EQ.7) NI=4
IF(II.EQ.8.OR.II.EQ.9) GO TO 1109
IF(II.EQ.10) GO TO 1110
GO TO (11,12,13,14) , NI
11 N=3*NI
M=1
NM=NI+1
DO 23 I=1,NM
DO 24 J=1,NM
A(I,J)=A40(J,I)
B(I,J)=B40(J,I)
B1(I,J)=B140(J,I)
24 QINV(I,J)=QINV40(J,I)
23 Z(I)=Z40(I)
GO TO 17
12 N=3*NI
M=1
NM=NI+1
DO 33 I=1,NM
DO 34 J=1,NM
A(I,J)=A41(J,I)
B(I,J)=B41(J,I)
B1(I,J)=B141(J,I)
34 QINV(I,J)=QINV41(J,I)
33 Z(I)=Z41(I)
GO TO 17
13 N=3*NI
M=1
NM=NI+1
DO 43 I=1,NM
DO 44 J=1,NM
A(I,J)=A42(J,I)
B(I,J)=B42(J,I)
B1(I,J)=B142(J,I)
44 QINV(I,J)=QINV42(J,I)

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43  Z(I)=Z42(I)
    GO TO 17
14  N=3*NI
    M=1
    NM=NI+1
    DO 53 I=1,NM
    DO 54 J=1,NM
    A(I,J)=A43(J,I)
    B(I,J)=B43(J,I)
    B1(I,J)=B143(J,I)
54  QINV(I,J)=QINV43(J,I)
53  Z(I)=Z43(I)
17  SN=(RNS-RNE)/(XS-XEQ)
    BN=RNS-SN*XS
    SS6=(S6SUR-S6EQ)/(XS-XEQ)
    BS6=S6SUR-SS6*XS
    DO 602 J=1,NI
    SI=Z(J)*Z(J)
    JJ=J+2*(J-1)
    RHS=(SI*(1.E00-C1)+C1)*(1.E00-XS)/RNS
    X(JJ)=(1.E00-RHS*BN)/(1.E00+RHS*SN)
    X(JJ+1)=SS6*X(JJ)+BS6
    X(JJ+2)=SN*X(JJ)+BN
602 CONTINUE
525 NEQ=N
1109 CALL SNLEQ(RHS,TS,PRESS,X,PAR,.75E00,M,N,3,NI,YH2S,DF,NEQ)
    GO TO 1270
1110 CONTINUE
C IN THIS SECTION ONE POINT IS CONSIDERED FOR GETTING YI AND EFF.
  RKISI=.6546536707E00
  SI=(RKISI)*(RKISI)
  RHS=(SI*(1.E00-C1)+C1)*(1.E00-XS)/RNS
  Y(3)=(1.E00-RHS*BN)/(1.E00+RHS*SN)
  Y(1)=SS6*Y(3)+BS6
  Y(2)=SN*Y(3)+BN
C NOW SNLEQ IS CALLED TO SOLVE FOR X,S6,AND N FOR SPECIFIED SI.
  CALL SNLEQ(RHS,TS,PRESS,Y,PAR,1.E00,M,3,5,NI,YH2S,DF,3)
  XRKISI=Y(3)

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S6KISI=Y(1)
TMKISI=Y(2)
RRKISI=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,XRKISI,S6KISI,TMKISI)
C NOW KISI OPTIMUM IS ESTIMATED
RRATIO=RATES/RRKISI
SIR=1.0E00/SI
POWER=LOG(RRATIO)/LOG(SIR)
OPKISI=(1.E00+POWER)**(.5E00/POWER)
OPKISI=1.E00/OPKISI
SI=OPKISI**2
RHS=(SI*(1.E00-C1)+C1)*(1.E00-XS)/RNS
Y(3)=(1.E00-RHS*BN)/(1.E00+RHS*SN)
Y(1)=SS6*Y(3)+BS6
Y(2)=SN*Y(3)+BN
CALL SNLEQ(RHS,TS,PRESS,Y,PAR,1.E00,M,3,5,NI,YH2S,DF,3)
XRKISI=Y(3)
S6KISI=Y(1)
TMKISI=Y(2)
RRKISI=RATE(PSH2O,PSSO2,NTYPE,TS,PRESS,PAR,XRKISI,S6KISI,TMKISI)
AYI=9.E00*(FIMOD**2)*RRKISI/RATES
CALL SOLYI(YI,RKISI,AYI,NFLAG)
EFF(II)=2./3./(FIMOD**2)/(1.-YI)
NI=1
GO TO 2000
1270 EFF(II)=A(NM,NM)
DO 1200 J=1,NI
K=J+2*(J-1)
1150 EFF(II)=EFF(II)+A(NM,J)/(1.-C1)*((1.-X(K))/(1.-XS)*RNS/X(K+2)-C1)
1200 CONTINUE
EFF(II)=EFF(II)/3./FIMOD/FIMOD
2000 CONTINUE
RETURN
END

```

EXAMPLE OF RUNNING THE PROGRAM "SMCLAUS.FOR"

INPUTS TO THE PROGRAM:

ENTER YH2S,YSO2,YH2O,YN2 (mol%)
 0.70000E-01 0.35000E-01 0.22500E+00 0.64000E+00
 ENTER YS2,YS4,YS6,YS8 (mol%)
 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00
 ENTER TF0(K),PRESS(atm)
 0.52300E+03 0.10000E+01
 ENTER DH2SM,DSO2M,DH2OM,DS6M,VIS,TCON
 0.44700E+00 0.34200E+00 0.43000E+00 0.13100E+00 0.25200E-03 0.94100E-04
 ENTER DHS,DSO,DW,DS6
 0.29200E-02 0.21300E-02 0.39000E-02 0.11400E-02
 ENTER VS0
 0.27800E+02
 ENTER DP,EB,DENB,DENP
 0.60000E+00 0.50000E+00 0.10000E+01 0.18500E+01
 ENTER GUESS VALUE X(1), X(2), X(3)
 .2,.5,.7,
 ENTER DELTH (cm)
 .5

Z	XF	XS	TF	TS	RATES	FIMOD	ETA
0.00	0.000000	0.000000	523.000000	523.000000	0.000014	7.818411	0.115713
1.00	0.035348	0.062679	526.826904	529.770020	0.000014	7.872211	0.115006
10.00	0.298112	0.319244	555.276855	557.301758	0.000010	8.541258	0.106912
20.00	0.486312	0.499992	575.653564	576.869141	0.000006	8.450595	0.107939
30.00	0.595477	0.603486	587.473145	588.154053	0.000003	7.439238	0.120978
40.00	0.654514	0.658812	593.865234	594.218750	0.000001	5.539653	0.158421
50.00	0.683225	0.684887	596.973633	597.118652	0.000000	2.959975	0.290006
60.00	0.692007	0.692125	597.924561	597.938965	0.000000	0.658598	0.788081
70.00	0.692363	0.692480	597.963135	597.968262	0.000000	0.025388	1.000000
80.00	0.692364	0.692481	597.963135	597.968262	0.000000	0.012694	1.000000
90.00	0.692364	0.692481	597.963135	597.968262	0.000000	0.012694	1.000000
100.00	0.692364	0.692481	597.963135	597.968262	0.000000	0.012694	1.000000

SATRT TO EVALUATE CONVERSIONS OF CS2 AND COS HYDROLYSIS IN THE SIMULATION CLAUS CONVERTER

ENTER CHARACTERISTIC PARTICLE SIZE (Lp), cm
 .1,
 ENTER INLET CS2 AND COS CONCENTRATION, mol%
 .7999998E-01,.1,
 ENTER DEACTIVATION DEGREE: ALFA, BETA0 AND FKK, %
 .7,.5,.8,
 SPHERICAL KAISER 201 (UNIFORM AND SHELL POISONING)
 ALFA=.7, BETA0=.5, AND FKK=.8,

TIME(S)	TEMP(K)	CS2(mol/mL)	COS(mol/mL)	CONV%	ETACS2	ETACOS	BETA
0.00000	523.00000	0.08000	0.10000	0.00000	0.02942	0.00938	0.50000
0.18000	540.78394	0.07948	0.09959	0.51333	0.04447	0.01473	0.65636
0.36000	555.27686	0.07854	0.09889	1.42740	0.05864	0.02070	0.76382
0.54000	566.76001	0.07708	0.09776	2.86841	0.07353	0.02774	0.83767
0.72000	575.65356	0.07501	0.09604	4.96795	0.08959	0.03611	0.88843

0.90000	582.41577	0.07230	0.09359	7.83877	0.10650	0.04576	0.92332
1.08000	587.47314	0.06897	0.09025	11.54200	0.12346	0.05639	0.94730
1.26000	591.19067	0.06511	0.08599	16.05457	0.13951	0.06742	0.96378
1.44000	593.86523	0.06088	0.08086	21.25551	0.15384	0.07816	0.97511
1.62000	595.73730	0.05643	0.07507	26.94151	0.16595	0.08796	0.98289
1.80000	596.97363	0.05194	0.06889	32.86838	0.17576	0.09641	0.98824
1.98000	597.65747	0.04755	0.06261	38.79814	0.18353	0.10337	0.99192
2.16000	597.92456	0.04335	0.05648	44.53549	0.18957	0.10889	0.99445
2.34000	597.96216	0.03941	0.05068	49.94623	0.19413	0.11311	0.99618
2.52000	597.96313	0.03576	0.04532	54.95599	0.19742	0.11621	0.99738
2.70000	597.96313	0.03240	0.04044	59.53612	0.19974	0.11843	0.99820
2.88000	597.96313	0.02932	0.03604	63.68742	0.20136	0.12001	0.99876
3.06000	597.96313	0.02652	0.03210	67.42847	0.20249	0.12112	0.99915
3.24000	597.96313	0.02398	0.02860	70.78749	0.20327	0.12189	0.99941
3.42000	597.96313	0.02167	0.02549	73.79700	0.20382	0.12243	0.99960
3.60000	597.96313	0.01958	0.02274	76.49010	0.20419	0.12280	0.99972

START TO EVALUATE CONCENTRATION DISTRIBUTIONS
THE CATALYST GEOMETRY IS SPHERICAL
ENTER TEMPERATURE (K) OF THE PARTICLE

523.,

ENTER DIAMETER (cm) OF THE PARTICLE

.6,

CS2 mol% DISTRIBUTION IN THE PARTICLE

R= 0.027 0.054 0.082 0.109 0.136 0.163 0.191 0.218 0.245 0.273

C= 0.008 0.010 0.014 0.022 0.035 0.058 0.099 0.173 0.306 0.551

COS mol% DISTRIBUTION IN THE PARTICLE

R= 0.027 0.054 0.082 0.109 0.136 0.163 0.191 0.218 0.245 0.273

C= 0.002 0.003 0.004 0.006 0.010 0.018 0.034 0.067 0.149 0.365

START TO EVALUATE CONCENTRATION DISTRIBUTIONS
THE CATALYST GEOMETRY IS SOLID CYLINDER
ENTER TEMPERATURE OF THE PARTICLE

523.,

ENTER HEIGHT OF THE CYLINDER (cm)

.524,

ENTER DIAMETER OF THE CYLINDER (cm)

.524,

CS2 mol% DISTRIBUTION

R= 0.024 0.048 0.072 0.095 0.119 0.143 0.167 0.191 0.214 0.238

H= 0.024 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.048 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.071 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.095 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.119 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.143 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.167 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.191 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.214 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

H= 0.238 0.012 0.014 0.019 0.028 0.043 0.069 0.114 0.193 0.331 0.574

COS mol% DISTRIBUTION

R=	0.023	0.047	0.071	0.095	0.119	0.142	0.166	0.190	0.214	0.238
H= 0.024	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.048	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.071	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.095	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.119	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.143	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.167	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.191	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.214	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370
H= 0.238	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.079	0.370

START TO EVALUATE CONCENTRATION DISTRIBUTIONS

THE CATALYST GEOMETRY IS A HOLLOW CYLINDER

ENTER TEMPERATURE OF THE PARTICLE

523.,

ENTER HEIGHT OF THE HOLLOW CYLINDER

.545,

ENTER OUTSIDE DIAMETER OF THE HOLLOW CYLINDER

.545,

ENTER THE HOLLOW DIAMETER OF THE HOLLOW CYLINDER

.182,

CS2 mol% DISTRIBUTION

R=	0.107	0.124	0.140	0.157	0.173	0.190	0.206	0.223	0.239	0.256
H= 0.025	0.620	0.399	0.274	0.210	0.188	0.200	0.247	0.332	0.470	0.682
H= 0.050	0.620	0.399	0.274	0.210	0.188	0.201	0.247	0.333	0.470	0.682
H= 0.074	0.621	0.400	0.275	0.211	0.189	0.202	0.248	0.333	0.471	0.682
H= 0.099	0.622	0.402	0.277	0.213	0.192	0.204	0.250	0.335	0.472	0.683
H= 0.124	0.623	0.405	0.282	0.218	0.197	0.209	0.254	0.339	0.475	0.684
H= 0.149	0.627	0.412	0.291	0.229	0.208	0.220	0.264	0.346	0.480	0.687
H= 0.173	0.636	0.427	0.310	0.251	0.231	0.242	0.284	0.363	0.492	0.692
H= 0.198	0.654	0.459	0.351	0.297	0.279	0.288	0.326	0.398	0.517	0.706
H= 0.223	0.693	0.526	0.437	0.393	0.378	0.386	0.416	0.474	0.573	0.736
H= 0.248	0.782	0.673	0.619	0.592	0.584	0.588	0.605	0.640	0.701	0.808

COS mol% DISTRIBUTION

R=	0.107	0.124	0.140	0.157	0.173	0.190	0.206	0.223	0.239	0.256
H= 0.025	0.379	0.111	0.015	0.000	0.000	0.000	0.000	0.040	0.164	0.474
H= 0.050	0.379	0.111	0.015	0.000	0.000	0.000	0.000	0.040	0.164	0.474
H= 0.074	0.379	0.111	0.015	0.000	0.000	0.000	0.000	0.039	0.164	0.474
H= 0.099	0.379	0.111	0.015	0.000	0.000	0.000	0.000	0.039	0.164	0.473
H= 0.124	0.379	0.110	0.014	0.000	0.000	0.000	0.000	0.038	0.164	0.473
H= 0.149	0.379	0.110	0.013	0.000	0.000	0.000	0.000	0.038	0.163	0.473
H= 0.173	0.380	0.111	0.014	0.000	0.000	0.000	0.000	0.038	0.163	0.474
H= 0.198	0.385	0.120	0.027	0.000	0.000	0.000	0.003	0.048	0.168	0.473
H= 0.223	0.401	0.168	0.091	0.065	0.058	0.059	0.069	0.100	0.191	0.453
H= 0.248	0.417	0.386	0.363	0.351	0.347	0.347	0.349	0.351	0.335	0.231